metal-organic papers

[(−)-α-Isosparteine]dinitratocopper(II)

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Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.014 Å
R factor = 0.055
wR factor = 0.129
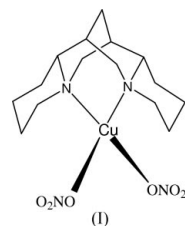Data-to-parameter ratio = 10.5

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

In the title compound, $[Cu(NO_3)_2(C_{15}H_{26}N_2)]$, the Cu atom is coordinated by the two N atoms of the bidentate (−)-α-isosparteine (Sp) ligand and by two O atoms from two nitrate anions, forming a distorted tetrahedron; the two nitrate ligands are coordinated to the Cu atom in a monodentate mode. The dihedral angle between the $N_{Sp}/Cu/N_{Sp}$ and $O_{nitrate}/Cu/O_{nitrate}$ planes is 27.7 (4)°.

Comment

In recent years, a large number of new transition metal complexes with sparteine groups have been reported, with various anionic ligands. These complexes show structurally interesting features around the metal atoms as a result of the bulky sparteine group. The sparteine has two coordinating sites through N atoms. The highly distorted geometry around the metal is due to the rigid relative positions of the two N atoms in the sparteine group. The chiral diamine alkaloid, sparteine $(C_{15}H_{26}N_2)$ has three diastereoisomers, namely (6R,7S,8S,14S)-(−)-L-sparteine, (6R,7S,8S,14R)-(−)-α-isosparteine and (6R,7S,8S,14S)-(−)-β-isosparteine, 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). Among the known copper(II) sparteine complexes, copper(II) L-sparteine dinitrate is unique with respect to its reactivity (Lee et al., 2002) and crystal structures (Choi et al., 1995); the nitrate ligand coordinated to copper(II) in this complex is substitutionally very labile, and L-sparteine copper(II) dinitrate has been used as a precursor compound for the preparation of many L-sparteine copper(II) complexes (Lee et al., 2002). This compound crystallizes in two different forms. The molecules of copper (II) L-sparteine dinitrate are mixed four- and five-coordinate in one crystalline phase and only four-coordinate in the other (Choi et al., 1995). The situation of the nitrate ligand being sometimes monodentate and sometimes bidentate in copper(II) L-sparteine dinitrate is very unusual.
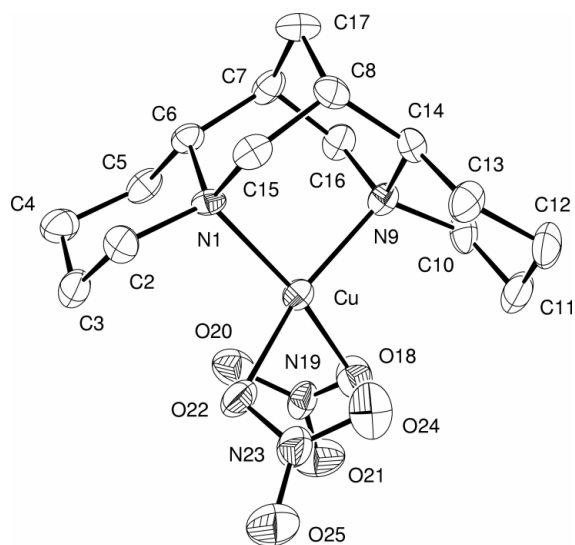

The crystal structure of the title compound, (I), has been analyzed in order to investigate the influence of the bulky α-

Figure 1
A view of (I), showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

isosparteine ligand on the molecular structure and the coordinating mode of the versatile nitrate anions. Kimblin *et al.* (2000) have studied intensively the effect of the nitrate ligand coordination modes in metalloenzymes by X-ray diffraction studies. The activities of metal-substituted carbonic anhydrases are related to the nitrate ligand coordination modes. For asymmetrical geometries, the coordination modes of the nitrate are classified as monodentate, anisobidentate and bidentate depending on the differences of both the $M-O$ bond distances and $M-O-N$ angles. The pertinent criteria for the monodentate mode are > 0.6 Å and $> 28°$ for the differences of bond distances and angles, respectively (Kleywegt *et al.*, 1985).

In complex (I) (Fig. 1), the Cu—O18 and Cu—O22 bond distances are 2.019 (8) and 1.974 (7) Å, respectively, and these are within the normal range of strong Cu—O(NO₃) interactions (Thompson *et al.*, 1995). The Cu—O20 [2.665 (7) Å] and Cu—O24 [2.636 (7) Å] distances are quite long. The calculated differences of short and long Cu—O bond distances for the nitrate ligands are 0.65–0.66 Å, and the calculated differences for the Cu—O—N angles are 32.1 and 31.4° in the two coordinated nitrate ligands. According to the above criteria, nitrate ligands are coordinated to the Cu atom in a monodentate mode, and the coordination geometry around the Cu^{II} center is four-coordinate pseudo-tetrahedral. The Cu—N(sparteine) distances of 2.007 (8) and 2.051 (9) Å are similar to those observed for analogous sparteine copper complexes (Lee, Kang *et al.*, 2003; Lee, Kwon *et al.*, 2003; Kim *et al.*, 2002). The dihedral angle between the N1/Cu/N9 and O18/Cu/O22 planes is 27.7 (4)° for the title compound, where a dihedral angle of zero would result in a planar inner coordination geometry. The majority of four-coordinate copper(II) complexes prefer to adopt a planar structure as a natural consequence of the d^9 configuration, and the distortion from the planar structure is due to the coordination of a bulky bidentate α-isosparteine to the Cu^{II} atom. The dihedral angle

of the title compound is smaller than the corresponding dihedral angle of 31.7° reported for the four-coordinate L-sparteine copper(II) dinitrate (Choi *et al.*, 1995). This result clearly indicates that the steric effect of α-isosparteine operating on the inner coordination sphere is less severe than that of L-sparteine. One of the major reasons for the distortion is the small N1—Cu—N2 angle of 89.7 (3) Å, which is due to the rigid relative positions of the N atoms in the sparteine group.

Experimental

(−)-α-Isosparteine was derived from available (−)-L-sparteine according to the literature method (Leonard & Beyler, 1950). The title copper(II) complex, [Cu(NO₃)₂(C₁₅H₂₆N₂)], was prepared in a glove-box by mixing a solution of copper(II) nitrate in ethanol–triethyl orthoformate (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. Single crystals were obtained by recrystallization, at about 278 K, from a solution in dichloromethane–triethyl orthoformate (5:1, v/v) under carbon tetrachloride vapor (m.p. 425 K). Analysis found: C 42.08, H 6.68, N 13.02%; calculated for C₁₅H₂₆CuN₄O₆: C 42.70, H 6.21, N 13.28%. IR (cm⁻¹): 1495 (vs, v_s, NO₃), 1290 (vs, v_a, NO₃), 1276 (vs, v_a, NO₃).

Crystal data

[Cu(NO₃)₂(C₁₅H₂₆N₂)]	Mo $K\alpha$ radiation
$M_r = 421.94$	Cell parameters from 40
Orthorhombic, $P2_12_12_1$	reflections
$a = 8.4920$ (15) Å	$\theta = 6.0–12.8°$
$b = 12.241$ (2) Å	$\mu = 1.28$ mm⁻¹
$c = 16.961$ (3) Å	$T = 293$ (2) K
$V = 1763.1$ (5) Å³	Block, blue
$Z = 4$	$0.38 \times 0.34 \times 0.28$ mm
$D_x = 1.59$ Mg m⁻³	

Data collection

Bruker $P4$ diffractometer	$R_{int} = 0.040$
$2\theta/\omega$ scans	$\theta_{max} = 26°$
Absorption correction: ψ scan	$h = -1 \rightarrow 10$
(North *et al.*, 1968)	$k = -15 \rightarrow 1$
$T_{min} = 0.620$, $T_{max} = 0.697$	$l = -20 \rightarrow 1$
2632 measured reflections	3 standard reflections
2451 independent reflections	every 97 reflections
1263 reflections with $I > 2\sigma(I)$	intensity decay: 2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.045P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.055$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.129$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.97$	$\Delta\rho_{max} = 0.49$ e Å⁻³
2451 reflections	$\Delta\rho_{min} = -0.53$ e Å⁻³
233 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	453 Friedel pairs
	Flack parameter = −0.03 (4)

Table 1
Selected geometric parameters (Å, °).

Cu—O22	1.974 (7)	Cu—N1	2.051 (8)
Cu—N9	2.007 (8)	Cu—O24	2.636 (7)
Cu—O18	2.019 (8)	Cu—O20	2.665 (7)
N9—Cu—N1	89.7 (3)	N23—O22—Cu	111.1 (7)
N19—O18—Cu	109.6 (8)	N23—O24—Cu	79.7 (6)
N19—O20—Cu	77.5 (6)		

H atoms of the sparteine ligand were positioned geometrically and constrained to ride on their attached atoms, with U_{iso}(H) values set at

$1.2U_{eq}$ of the parent atoms. The absolute configuration of (I) was known from the configuration of the starting material and was confirmed by the value [−0.03 (4)] 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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