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References

- Bright, D. & Mills, O. S. (1967). *Chem. Commun.* pp. 245–246.
 Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
 Gervasio, G., Stanghellini, P. L. & Rossetti, R. (1981). *Acta Cryst.* B37, 1198–1202.
 Nametkin, N. S., Tyurin, V. D., Trusov, V. V., Nekhaev, A. I., Batsanov, A. S. & Struchkov, Yu. T. (1986). *J. Organomet. Chem.* 302, 243–248.
 Nardelli, M. (1995). *J. Appl. Cryst.* 28, 659.
 Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* University of Cambridge, England.
 Sheldrick, G. M. (1990). *Acta Cryst.* A46, 467–473.
 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
 Siemens (1991a). *P3/P4-PC Diffractometer Program.* Version 4.27. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Siemens (1991b). *XDISK. Data Reduction Program.* Version 4.20.2PC. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Zimniak, A. (1992). *Pol. J. Chem.* 66, 1051–1057.
 Zimniak, A. & Buczkowski Z. (1980). *Bull. Acad. Pol. Sci. (Chem.)*, 28, 365–370.
 Zimniak, A. & Buczkowski Z. (1982). *Bull. Acad. Pol. Sci. (Chem.)*, 29, 231–237.
 Zimniak, A. & Zachara, J. (1997). *J. Organomet. Chem.* 533, 45–49.

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Dichloro[(-)-sparteine-*N,N'*]copper(II)

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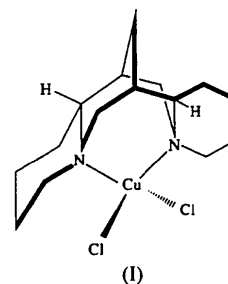
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Abstract

In the title compound, $[\text{CuCl}_2(\text{C}_{15}\text{H}_{26}\text{N}_2)]$, the bulky fused rings of the sparteine ligand induce a pseudo-tetrahedral environment around the copper(II) atom. All four alkaloid rings adopt the chair conformation, with one terminal ring inclined *endo* (pointing towards the metal atom) and the other inclined *exo* (pointing away from the metal). The main dimensions of the complex include Cu–N 2.003 (3) and 2.021 (3), Cu–Cl 2.238 (1) and 2.258 (1) Å, N–Cu–N 90.5 (2) and Cl–Cu–Cl 106.92 (6)°.

Comment

Metal complexes of sparteine alkaloids (Mason & Peacock, 1973) are useful reagents in organic synthesis. The bulky chiral sparteine ligand creates asymmetry around the metal atom, and can induce varying degrees of enantiomeric purity when used in certain addition reactions (Beak *et al.*, 1996; Kretschmer, 1972). The exact geometry of the complexes, and in particular the steric accessibility to the metal center, is the key to their successful application. The current compound, (I), was isolated during our ongoing study of copper-catalyzed asymmetric zinc addition reactions (Jansen & Feringa, 1990; Ukaji *et al.*, 1996).



The four-ring natural alkaloid (–)-sparteine has two additional diastereomers, α -isosparteine and β -isosparteine, which are distinguished by the different orientations of their two terminal rings (Boschmann *et al.*, 1974). The crystal structure of the Cu^{II} chloride adduct of β -isosparteine has been reported previously (Childers *et al.*, 1975), in which the ligand retains its original conformation when coordinated to the metal. The structures of the other two isomeric metal complexes have only been postulated from various spectroscopic (Choi *et al.*, 1975) and reactivity data (Cady *et al.*, 1977) of copper(II)–sparteine complexes, indicating the retention of conformation when each isomer chelates to metal cations.

A view of the molecular structure of the title compound is shown in Fig. 1. Copper(II) metal centers typically display an octahedral (Jahn–Teller distorted) coordination geometry. However, in both the copper complex of β -isosparteine (Childers *et al.*, 1975) and the present structure, the steric bulk of the bidentate sparteine ligand and the chloride anions lowers the coordination number to four, with a very compressed N–Cu–N angle of 90.5°. In addition, the tetrahedron is twisted, thereby further distorting the bond angles. The Cl1–Cu–Cl2 angle in Fig. 1 is 106.92 (6)°, close to the 109.5° angle in a perfect tetrahedron. All of the other angles about the copper(II) center deviate substantially from ideal [from 100.05 (11) to 134.13 (11)°]. The distorted coordination geometry is very similar to the dimethylzinc complex of (–)-sparteine (Motevalli *et al.*, 1993).

As predicted by previous investigators, the conformation of the dichloro[(-)-sparteine]copper(II) complex consists of one terminal ring folded down over the metal

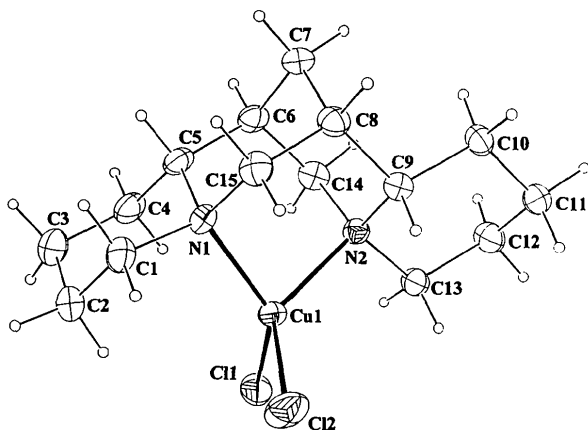


Fig. 1. The molecular structure of [CuCl₂(C₁₅H₂₆N₂)]; displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

(*endo*) and the other terminal ring folded back away from the metal (*exo*), identical to the conformation of the free ligand. One consequence of the *endo-exo* configuration is the slight asymmetry in the Cu—N bond lengths compared with the symmetric β -isosparteine-copper complex where both terminal rings point away from the metal. In that case, both Cu—N bond distances are 1.994 (6) Å (Childers *et al.*, 1975), whereas in the present complex, the nitrogen of the *endo* ring, N1, has a shorter Cu—N bond length, 2.002 (3) Å compared with 2.021 (3) Å for Cu—N2.

Experimental

[CuCl₂(C₁₅H₂₆N₂)] was prepared by first deprotonating CH₃-NO₂ with *n*-BuLi, and then reacting this with [Me₂S.CuBr], followed by the addition of (–)-sparteine. Compound (I) quickly precipitated out and was recrystallized by dissolution in CHCl₃ and allowing EtOAc to slowly diffuse into the mixture. Crystals began appearing after 2 d and were air stable. Melting-point determination shows that these crystals do not decompose before 538 K.

Crystal data

[CuCl₂(C₁₅H₂₆N₂)]

M_r = 368.82

Monoclinic

*P*2₁

a = 8.7286 (6) Å

b = 8.0635 (6) Å

c = 12.2610 (9) Å

β = 105.7900 (10)°

V = 830.40 (10) Å³

Z = 2

D_x = 1.475 Mg m^{–3}

D_m not measured

Mo *K*α radiation

λ = 0.71070 Å

Cell parameters from 5243 reflections

θ = 1.73–54.27°

μ = 1.629 mm^{–1}

T = 293 (2) K

Cubic

0.20 × 0.17 × 0.15 mm

Dark green

Data collection

Siemens SMART/CCD diffractometer

2834 reflections with *I* > 2σ(*I*)

ω scans

Absorption correction:

empirical (SADABS;

Sheldrick, 1996)

T_{min} = 0.270, *T_{max}* = 0.345

5243 measured reflections

3276 independent reflections

R_{int} = 0.032

θ_{\max} = 27.14°

h = –11 → 10

k = –9 → 10

l = 0 → 15

1321 standard reflections

frequency: 0.1667 min

intensity decay: none

Refinement

Refinement on *F*²

R(*F*) = 0.041

wR(*F*²) = 0.099

S = 1.022

3276 reflections

205 parameters

H atoms constrained

$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)_{max} = –0.018

$\Delta\rho_{\max}$ = 0.848 e Å^{–3}

$\Delta\rho_{\min}$ = –0.940 e Å^{–3}

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Absolute structure: Flack

(1983)

Flack parameter = 0.04 (2)

Table 1. Selected geometric parameters (Å, °)

Cu1—N1	2.003 (3)	Cu1—Cl1	2.2582 (13)
Cu1—N2	2.021 (3)	Cu1—Cl2	2.2375 (11)
Cl1—Cu1—Cl2	106.92 (6)	C1—N1—Cu1	110.2 (3)
N1—Cu1—Cl1	134.13 (11)	C5—N1—Cu1	109.5 (3)
N1—Cu1—Cl2	100.05 (11)	C15—N1—Cu1	109.4 (3)
N2—Cu1—Cl1	101.73 (12)	C9—N2—Cu1	107.1 (2)
N2—Cu1—Cl2	126.53 (9)	C13—N2—Cu1	104.7 (3)
N1—Cu1—N2	90.5 (2)	C14—N2—Cu1	109.4 (2)

H atoms were placed geometrically and refined using a riding model with *U*_{iso} constrained to be 1.2*U*_{eq} of the carrier atom.

Data collection: SMART (Siemens, 1995). Cell refinement: SMART and SAINT (Siemens, 1995). Data reduction: SHELXL93 (Sheldrick, 1993) and RES2INS (Barbour, 1996). Program(s) used to solve structure: SHELXL93. Molecular graphics: SHELXL93. Software used to prepare material for publication: SHELXL93.

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References

- Barbour, L. (1996). RES2INS. Graphical Interface Program for SHELXL. University of Missouri–Columbia, USA.
- Beak, P., Basu, A., Gallagher, D. J., Park, Y. S. & Thayumanavan, S. (1996). *Acc. Chem. Res.* **29**, 552–560.
- Boschmann, E., Weinstock, L. M. & Carmack, M. (1974). *Inorg. Chem.* **13**, 1297–1300.
- Cady, W. A., Boschmann, E., Choi, R. S., Heidelman, J. F. & Smith, S. L. (1977). *Inorg. Chem.* **16**, 1958–1961.
- Childers, L. S., Folting, K., Merrit, L. L. & Streib, W. E. (1975). *Acta Cryst.* **B31**, 924–925.
- Choi, S.-N., Bereman, R. D. & Wasson, J. R. (1975). *J. Inorg. Nucl. Chem.* **37**, 2087–2090.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Jansen, J. F. G. A. & Feringa, B. L. (1990). *J. Org. Chem.* **55**, 4168–4175.

- Kretchmer, R. A. (1972). *J. Org. Chem.* **37**, 2744–2747.
- Mason, S. F. & Peacock, R. D. (1973). *J. Chem. Soc. Dalton Trans.* pp. 226–228.
- Motevalli, M., O'Brien, P., Robinson, A. J., Walsh, J. R., Wyatt, P. B. & Jones, A. C. (1993). *J. Organomet. Chem.* **461**, 5–7.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
- Sheldrick, G. M. (1996). *SADABS. Siemens Area Detector Absorption Correction Software.* University of Göttingen, Germany.
- Siemens (1995). *SMART and SAINT. Area Detector Control and Integration Software.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Ukaji, Y., Kenmoku, Y. & Inomata, K. (1996). *Tetrahedron Asymm.* **7**, 53–56.