

Table 1. Selected geometric parameters (Å, °)

Mo1—C1	1.938 (5)	Mo2—C5	1.942 (5)
Mo1—C2	1.995 (5)	Mo2—C6	1.992 (6)
Mo1—C3	2.026 (6)	Mo2—C4	2.006 (5)
Mo1—O31	2.228 (3)	Mo2—O32	2.245 (3)
Mo1—S1	2.4527 (12)	Mo2—S1	2.4774 (12)
Mo1—S2	2.4809 (12)	Mo2—S2	2.4950 (13)
Mo1—Mo2	2.9115 (5)		
C1—Mo1—O31	175.5 (2)	C6—Mo2—S1	85.38 (14)
C2—Mo1—O31	100.5 (2)	C4—Mo2—S1	157.50 (14)
C3—Mo1—O31	87.8 (2)	O32—Mo2—S1	77.83 (8)
C1—Mo1—S1	98.9 (2)	C5—Mo2—S2	83.9 (2)
C2—Mo1—S1	82.72 (15)	C6—Mo2—S2	163.33 (15)
C3—Mo1—S1	158.9 (2)	C4—Mo2—S2	86.6 (2)
O31—Mo1—S1	77.95 (8)	O32—Mo2—S2	90.09 (8)
C1—Mo1—S2	85.99 (15)	S1—Mo2—S2	107.36 (4)
C2—Mo1—S2	164.8 (2)	C5—Mo2—Mo1	96.84 (15)
C3—Mo1—S2	87.12 (15)	C6—Mo2—Mo1	137.27 (14)
O31—Mo1—S2	92.01 (8)	C4—Mo2—Mo1	137.5 (2)
S1—Mo1—S2	108.60 (4)	O32—Mo2—Mo1	80.69 (8)
C1—Mo1—Mo2	93.22 (15)	S1—Mo2—Mo1	53.41 (3)
C2—Mo1—Mo2	135.55 (15)	S2—Mo2—Mo1	53.96 (3)
C3—Mo1—Mo2	139.60 (14)	C11—S1—Mo1	113.97 (15)
O31—Mo1—Mo2	82.34 (8)	C11—S1—Mo2	120.3 (2)
S1—Mo1—Mo2	54.20 (3)	Mo1—S1—Mo2	72.39 (3)
S2—Mo1—Mo2	54.41 (3)	C21—S2—Mo1	117.2 (2)
C5—Mo2—O32	173.9 (2)	C21—S2—Mo2	113.3 (2)
C6—Mo2—O32	103.4 (2)	Mo1—S2—Mo2	71.62 (3)
C4—Mo2—O32	84.8 (2)	C31—O31—Mo1	124.9 (3)
C5—Mo2—S1	105.29 (14)	C31—O32—Mo2	126.2 (3)

H atoms were all located theoretically and refined. Structure solution and refinement were carried out on an Indy workstation of a Silicon Graphics instrument with *SHELXTL/PC* (Sheldrick, 1994).

Data collection: *SMART* (Siemens, 1996). Cell refinement: local programs. Data reduction: *SAINT* (Siemens, 1994). Program(s) used to solve structure: *SHELXTL/PC*. Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXTL/PC* and local programs.

We are grateful to NNSF and SKLSC for financial support of this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1087). Services for accessing these data are described at the back of the journal.

References

- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Sheldrick, G. M. (1994). *SHELXTL/PC*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1996). *SADABS*. Program for Absorption Correction. University of Göttingen, Germany.
- Siemens (1994). *SAINT Reference Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1996). *SMART Reference Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Zhuang, B., Huang, L. & He, L. (1995). *Chin. J. Struct. Chem.* **14**, 359–363.
- Zhuang, B., Huang, L., He, L., Yang, Y. & Lu, J. (1987). *Inorg. Chim. Acta*, **127**, L7–8.
- Zhuang, B., Huang, L., He, L., Yang, Y. & Lu, J. (1989). *Acta Chim. Sin.* **47**, 25–30.

Acta Cryst. (1998). **C54**, 1582–1584

(–)-Sparteine Copper(II) Dinitrite†

YONG-MIN LEE,^a SUNG-NAK CHOI,^a IL-HWAN SUH^b AND ROBERT D. BEREMAN^c

^aDepartment of Chemistry, Pusan National University, Pusan 609-735, Korea, ^bDepartment of Physics, Chungnam National University, Taejon 305-764, Korea, and ^cDepartment of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204, USA. E-mail: sunachoi@hyowon.cc.pusan.ac.kr

(Received 18 August 1997; accepted 16 April 1998)

Abstract

The title complex, [Cu(NO₂)₂(C₁₅H₂₆N₂)], has been prepared and its crystal structure determined. The chiral nitrogen-chelating alkaloid (–)-sparteine acts as a bidentate ligand, reacting with one Cu^{II} ion in ethanol to form the title complex, with two nitrite groups occupying the remaining coordination sites to produce a distorted five-coordinate square-pyramidal structure. One nitrite is bound through one O atom and the other nitrite acts as a η²-chelating group.

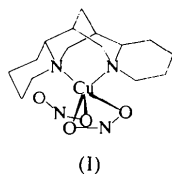
Comment

Over the past two decades, several studies of transition metal complexes of the neutral alkaloid (–)-sparteine (C₁₅H₂₆N₂) have been reported (Boschmann *et al.*, 1974, 1978; Fraencel *et al.*, 1974; Childers *et al.*, 1975; Wroblewski & Long, 1977), and the crystal and molecular structures of some sparteine metal complexes of the type [MX₂(C₁₅H₂₆N₂)] have been determined (Togni *et al.*, 1990; Choi *et al.*, 1995).

Previously, we determined the crystal structure of (–)-sparteine copper(II) dinitrate, and found that molecules of this compound are mixed four- and five-coordinate in one crystalline phase and only four-coordinate in the other (Choi *et al.*, 1995). These results indicate the near electronic energy equivalence of four- and five-coordination about Cu^{II} in this compound. This is a rare example of a pure compound which displays two different coordination numbers in the same crystalline structure.

The nitrite ion, like the nitrate ion, can coordinate to a metal in either a mono- or bidentate fashion, and we expected that (–)-sparteine copper(II) dinitrite, (I), might also exhibit similar structural features. However, the Cu^{II} ion in this complex is exclusively five-coordinate, with a highly distorted square-pyramidal geometry in

† Alternative name: {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'*}-dinitrito-*O,O'*-copper(II).



which one O atom of the bidentate nitrite ligand occupies the axial position. The basal plane is constituted by two N atoms of the (–)-sparteine, one O atom of the chelating nitrite ligand, and one O atom (O3) of the monodentate nitrite. The Cu—O1 and Cu—O3 distances are similar to those found for relatively strongly coordinated anions. The Cu—O2 distance reflects the fact that the metal—O_{axial} interaction is remarkably weak [2.402 (6) Å], as might be expected for the ‘axial’ bond distance. The Cu···O4 distance of 2.637 (5) Å is too long for this to be considered as a bonding interaction. The N1—Cu—N9 plane is twisted by 31.7° from the O1—Cu—O3 plane. The elongation of the axial Cu—O2 distance, and the virtual non-existence of any bonding interaction between the Cu and O4 atoms, are expected to be caused by Jahn–Teller distortion operating on the *d*⁹ system.

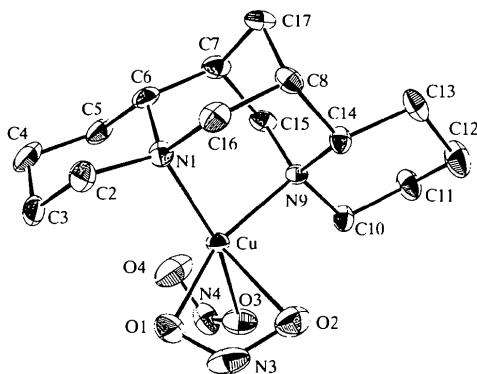


Fig. 1. ORTEPII (Johnson, 1976) diagram of [Cu(NO₂)₂(C₁₅H₂₆N₂)]. Non-H atoms are represented with 40% probability ellipsoids.

Experimental

The precursor metal complex, [Cu(NO₃)₂(C₁₅H₂₆N₂)], was prepared in a glove-box by mixing an ethanol–triethylorthoformate (5:1 *v/v*) solution of copper nitrate with a stoichiometric amount of (–)-sparteine. The resulting blue precipitate was filtered, washed with cold absolute ethanol and dried under vacuum. The title complex, [Cu(NO₂)₂(C₁₅H₂₆N₂)], was prepared by the nucleophilic substitution reaction of [Cu(NO₃)₂(C₁₅H₂₆N₂)] with a stoichiometric amount of NaNO₂ in ethanol–triethylorthoformate (5:1 *v/v*) solution. Single crystals were obtained by recrystallization at about 278 K from a dichloromethane–triethylorthoformate (5:1 *v/v*) solution under carbon tetrachloride vapour.

Crystal data

[Cu(NO₂)₂(C₁₅H₂₆N₂)]
M_r = 389.94
 Orthorhombic
*P*2₁2₁2₁
a = 12.288 (12) Å
b = 17.557 (14) Å
c = 7.960 (15) Å
V = 1717.3 (4) Å³
Z = 4
D_x = 1.508 Mg m^{–3}
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 11.29–13.61°
 μ = 1.299 mm^{–1}
T = 296 (2) K
 Cube
 0.30 × 0.30 × 0.26 mm
 Green

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 2839 measured reflections
 2839 independent reflections
 1445 reflections with $F^2 > 2\sigma(F^2)$

θ_{\max} = 29.97°
 h = 0 → 17
 k = 0 → 24
 l = 0 → 11
 3 standard reflections
 frequency: 240 min
 intensity decay: 0.8%

Refinement

Refinement on F^2
R = 0.057
wR = 0.084
S = 1.203
 2839 reflections
 217 parameters
 H atoms not refined
 $w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.50P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.342 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.298 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)
 Absolute structure: Flack (1983)
 Flack parameter = 0.05 (3)

Table 1. Selected geometric parameters (Å, °)

Cu—O1	2.025 (5)	Cu—O4	2.637 (5)
Cu—O2	2.402 (6)	Cu—N1	2.019 (6)
Cu—O3	2.002 (5)	Cu—N9	2.040 (4)
O1—Cu—O2	55.4 (2)	O2—Cu—N1	110.1 (2)
O1—Cu—O3	84.0 (2)	O2—Cu—N9	99.2 (2)
O1—Cu—N1	95.2 (2)	O3—Cu—N1	162.5 (2)
O1—Cu—N9	154.3 (2)	O3—Cu—N9	98.5 (2)
O2—Cu—O3	83.9 (2)	N1—Cu—N9	89.7 (2)

All non-H atoms were found by direct methods and their parameters were refined successfully with a full-matrix least-squares procedure. H atoms were geometrically positioned and fixed. Absorption corrections were not applied because the crystal shape was uniform. Some displacement ellipsoids elongated along the bonds might be attributable to this omission. The absolute configuration was confirmed.

Data Collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software*. Program used to solve structure: *SHELXS86* (Sheldrick, 1990). Program used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976) in *NRC-VAX* (Gabe *et al.*, 1989). Software used to prepare material for publication: *SHELXL93*.

This research was supported by the Korean–USA Cooperative Science Program, Korean Science and Engineering Foundation (1994.12–1996.11).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1191). Services for accessing these data are described at the back of the journal.

References

- Boschmann, E., Nypaver, G. A., Major, J. P., Ealy, S. M. & Vanhorn, M. (1978). *J. Coord. Chem.* **7**, 141–147.
- Boschmann, E., Weinstock, L. & Carmack, M. (1974). *Inorg. Chem.* **13**, 1297–1300.
- Childers, L. S., Foltz, K., Merritt, L. Jr & Streib, W. E. (1975). *Acta Cryst.* **B31**, 924–926.
- Choi, S.-N., Kwon, M. A., Kim, Y., Bereman, R. D., Singh, P., Knight, B. & Seff, K. (1995). *J. Coord. Chem.* **34**, 241–252.
- Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Fraencl, G., Appleman, B. & Ray, J. G. (1974). *J. Am. Chem. Soc.* **96**, 5113–5119.
- Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- 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.
- Togni, A., Rihs, G., Pregosin, P. S. & Ammann, C. (1990). *Helv. Chim. Acta*, **73**, 723–732.
- Wroblewski, J. T. & Long, G. J. (1977). *Inorg. Chem.* **16**, 704–709.

Acta Cryst. (1998). **C54**, 1584–1586

cis-(2,2'-Bipyridyl-*N,N'*)carbonyl(methanato-*C*)(η^2 -2,2':6',2''-terpyridyl-*N,N'*)-ruthenium(II) Hexafluorophosphate

DOROTHY H. GIBSON, BRADLEY A. SLEADD, MARK S. MASHUTA AND JOHN F. RICHARDSON

Department of Chemistry and, Center for Chemical Catalysis, University of Louisville, Louisville, KY 40292, USA. E-mail: dhgibs01@homer.louisville.edu

(Received 17 February 1998; accepted 5 May 1998)

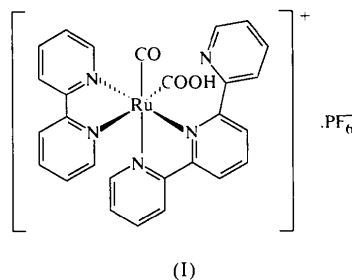
Abstract

The title compound, [Ru(CHO₂)(C₁₀H₈N₂)(C₁₅H₁₁-N₃)(CO)]PF₆ or *cis*-[Ru(bpy)(η^2 -tpy)(CO)(COOH)]PF₆ (where bpy is 2,2'-bipyridyl and tpy is 2,2':6',2''-terpyridyl), has distorted octahedral geometry about the Ru atom, a bidentate terpyridyl ligand and a fully chelated bipyridyl ligand. The terminal carbonyl and carboxyl groups are *cis*. The Ru—C—O angle (terminal carbonyl) is distorted from linearity [173.7 (4)°] by the pendant pyridyl group of the *N,N'*-bound tpy ligand, which is hydrogen bonded to the hydroxyl proton of the carboxyl group.

Comment

In spite of their importance as intermediates in water-gas shift (WGS) reactions (Ford, 1993) and in metal-catalyzed carbon dioxide conversions (Sutin *et al.*, 1997), only two metallocarboxylic acids, MCOOH, have been structurally characterized. The platinum complexes, *trans*-[Pt(Ph)(PEt₃)₂(COOH)] (Bennett *et al.*, 1988) and [Pt(COOH){C₆H₃(CH₂PPh₂)₂-2,6}] (Bennett *et al.*, 1993) exist as dimers, resulting from hydrogen bonding involving the carboxyl groups. A ruthenium complex, *cis*-[Ru(bpy)₂(CO)(COOH)](CF₃SO₃) (Toyohara *et al.*, 1996), showed hydrogen bonding of the carboxyl protons of two molecules of the acid to the oxygen of a bridging water molecule.

We prepared the title compound, (I), because of the importance of such ruthenium complexes in catalytic conversions of carbon dioxide (Sutin *et al.*, 1997).



Compound (I) exists as a monomer with distorted octahedral geometry about the Ru atom. Its formulation as a metallocarboxylic acid follows from its IR spectral

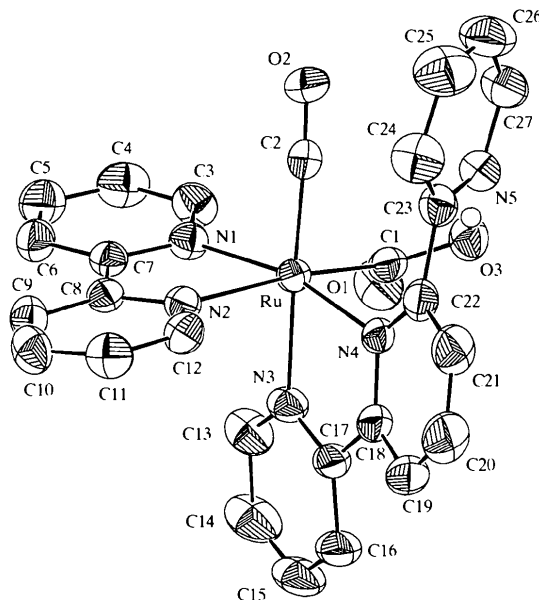


Fig. 1. ORTEPII (Johnson, 1976) plot of the title complex (cation only) showing 50% probability displacement ellipsoids. H atoms (with the exception of HO3) have been omitted for clarity.