Tetrahedral Distortion in Copper(II) Complexes of (–)-Sparteine and Its Effect on the Oxygen Adduct Formation

Yasuhiro Funahashi,*[†,††] Kaori Nakaya,[††] Shun Hirota,[††] and Osamu Yamauchi*[††,†††]
[†]*Research Center for Molecular Materials, Institute for Molecular Science, Myodaiji, Okazaki 444-8585*
[††]*Department of Chemistry, Graduate School of Science, Nagoya University, Chikusa-ku, Nagoya 464-8602*
[†††]*Unit of Chemistry, Faculty of Engineering, Kansai University, Yamate-cho, Suita, Osaka 564-8680*

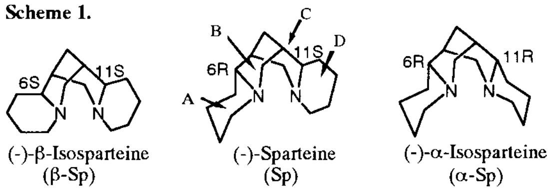
(Received July 25, 2000; CL-000703)

The Cu(II) complexes of (–)-sparteine (Sp) have been revealed to have tetrahedrally distorted structures in both monomeric and hydroxo-bridged dimmeric forms due to the steric requirements of Sp. Resonance Raman and UV absorption spectra indicated that the Cu(I) complex of Sp reacted with O_2 at –80 °C to form a distorted $Cu^{III}_2(\mu\text{–}O)_2$ structure.

Biomimetic model studies established that the binuclear copper site in oxyhemocyanin has a side-on ($\mu\text{–}\eta2{:}\eta2$) peroxo dicopper(II) structure.[1] Extensive studies on the Cu–dioxygen complexes further revealed the interconversion between $\mu\text{–}\eta2{:}\eta2$–peroxodicopper(II) and bis(μ-oxo) dicopper(III) cores,[2a] and their structure–reactivity relationship has been subject of biological interest in recent years.[2,3] The $Cu^{III}_2(\mu\text{-}O)_2$ structures so far reported have a planer "diamond" structure, but tetrahedral distortion of the core structure may give rise to unique spectral and redox chemical properties.

We report herewith synthesis of a monomeric complex and a bis(μ-hydroxo)-bridged dimeric copper(II) complex and a $Cu^{III}_2(\mu\text{-}O)_2$ core by using a lupin alkaloid from *Spartium scoparium*, (–)-sparteine (Sp)[4] (Scheme 1), which coordinates to Cu(II) as a bidentate ligand to produce a tetrahedrally distorted geometry around the Cu center.[5,6] The structures of the Cu(II) complexes have been determined by the X-ray diffraction method, and formation of the $Cu^{III}_2(\mu\text{-}O)_2$ core by oxygenation of the Cu(I) complex has been established by spectroscopic methods.

Scheme 1.



$[Cu^{II}(Sp)]Cl_2$ (**1**) was synthesized by mixing equimolar amounts of $CuCl_2{\cdot}2H_2O$ and Sp in hot ethanol as green crystals.[5,6] The molecular structure of **1** (Figure 1)[7] shows that the Cu(II) ion has a distorted tetrahedral geometry, which has been suggested by spectroscopic and redox properties (λ_{max} = 780 nm (ε = 184 M^{-1} cm^{-1}; M = mol dm^{-3}),[6a] $g_{//}$ = 2.30, $|A_{//}|$ = 9.0 mT,[6b] and $E_{1/2}$ (in DMSO) = 0.13 V (vs Ag/AgCl)).

$[(Sp)_2Cu^{II}_2(OH)_2](ClO_4)_2$ (**2**) was synthesized as green crystals in ethanol by oxidation of a solution containing $[Cu^I(CH_3CN)_4]ClO_4$ and Sp with O_2 at room temperature. The molecular structure of **2** (Figure 2) shows that the two Cu(II) centers form a hydroxo-bridged $M_2(\mu\text{-}OH)_2$ core structure, where the coordination planes are twisted.

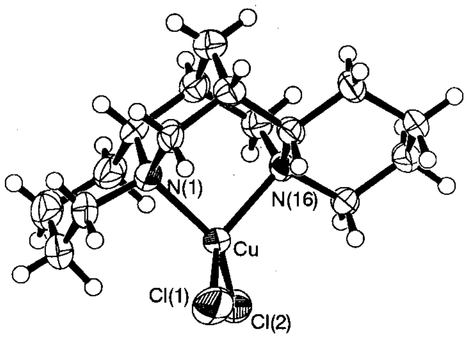


Figure 1. ORTEP drawing of **1** with thermal ellipsoids drawn at the 50% probability. Selected bond distances (Å) and angles (°): Cu-N(1) 1.993(5), Cu-N(16) 2.017(5), Cu-Cl(1) 2.262(2), Cu-Cl(2) 2.224(2), N(1)-Cu-N(16) 90.5(2), N(1)-Cu-Cl(1) 101.2(2), Cl(1)-Cu-Cl(2) 105.60(8), N(1)-Cu-Cl(2) 134.9(2), N(16)-Cu-Cl(1) 121.9(2), N(16)-Cu-Cl(2) 104.7(2).

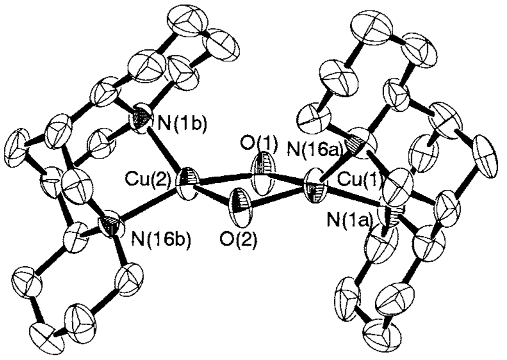


Figure 2. ORTEP drawing of **2** with thermal ellipsoids drawn at the 50% probability. The hydrogen atoms are omitted for clarify. Selected bond distances (Å) and angles (°): Cu(1)-N(1a) 1.98(1), Cu(1)-N(16a) 2.03(1), Cu(2)-N(1b) 2.02(1), Cu(2)-N(16b) 2.02(1), Cu(1)-O(1) 1.925(9), Cu(1)-O(2) 1.93(1), Cu(2)-O(1) 1.909(10), Cu(2)-O(2) 1.951(10), N(1a)-Cu(1)-N(16a) 90.6(5), N(1a)-Cu(1)-O(1) 103.0(5), N(16a)-Cu(1)-O(2) 105.6(5), O(1)-Cu(1)-O(2) 79.5(4), N(1b)-Cu(2)-N(16b) 90.3(5), N(1b)-Cu(2)-O(1) 101.2(5), N(16b)-Cu(2)-O(2) 101.4(5) O(1)-Cu(2)-O(2) 79.4(4).

The projection view of the Cu(II) coordination geometry on a plane perpendicular to the pseudo-C_2 rotation axis of **1** is shown in Figure 3a. In the structure of **1**, Sp has A ring folded down over and D ring folded back away from the metal and the respective major and minor steric constraints of A and D rings gave the different tortional distortion angles from orthogonality (17.5° and 25.6° for Cu–Cl(1) and Cu–Cl(2), respectively) (Figure 3a). In the case that both A and D rings simultaneously folded outwards and the major steric constraint of A ring disappeared, the coordination geometry becomes close to intrinsic tetrahedral as shown in the structure of Cu(II) dichloride complex with (–)-β-isosparteine (Scheme 1), the tortional distortion angles being 3°.[5a]

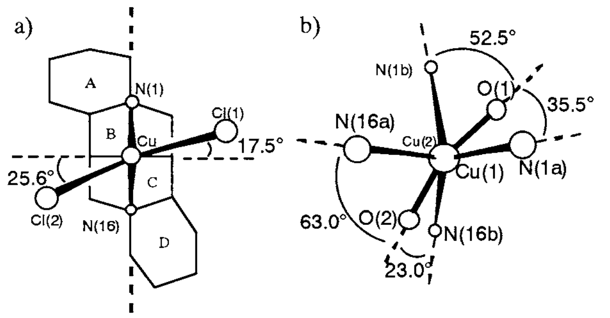


Figure 3. Projection views of a) molecular structure of **1** on the plane perpendicular to pseudo-C_2 axis and b) coodination structure of **2** on the plane perpendicular to the Cu(1)-Cu(2) axis.

The projection view of the coordination on a plane perpendicular to the Cu(1)–Cu(2) axis of **2** shows that both N(1)–Cu–N(16) planes crossed orthogonally and a $Cu_2(\mu\text{-}OH)_2$ plane was held in the middle (Figure 3b).

The structures of **1** and other metal complexes of three stereoisomers[5] prove that the tetracyclic structure of the alkaloids essentially induces the Cu(II) center to assume the tetrahedral coordination regardless of Jahn–Teller effect. It seems likely that the multi-linked sp^3 bond network of sparteine fixes its two nitrogen atoms favorably for tetrahedral coordination. The Cu(II) geometry of **2** is also affected by the tetrahedral distortion, when Cu(II) complexes with Sp form bridged dimer structures.

Sp reacts with one equivalent of $[Cu^I(CH_3CN)_4]CF_3SO_3$ in THF, giving crystalline products of $[Cu^I(Sp)(CH_3CN)_2]CF_3SO_3$ (**3**). Addition of O_2 through a clear solution of **3** in CH_2Cl_2 at –80 °C oxygenated the Cu(I) complex immediately in a 2:1 ($Cu:O_2$) stoichiometry, and the solution color changed to yellow–brown. The corresponding UV–Vis spectrum showed intense absorption bands centered at λ_{max} (ε / M^{-1} cm^{-1} $(2Cu)^{-1}$) = 330 nm (12500) and 427 nm (22800) (Table 1). The resonance Raman (rR) spectrum of the oxygenated solution of **3** with $^{16}O_2$ in CH_2Cl_2 at –80 °C exhibited an intense band at 619 cm^{-1}, which shifted to 591 cm^{-1} when $^{18}O_2$ was used (514.5 nm laser excitation). Observation of the oxygen-isotope-sensitive band demonstrated formation of a O_2 adduct of Cu for the oxygenated solution of **3**. The frequency and ^{18}O-isotope shift of the 619-cm^{-1} band ($\Delta\nu$ = 28 cm^{-1}) are characteristic of the totally symmetric mode of the $Cu^{III}{}_2(\mu\text{-}O)_2$ core in Cu complexes,[2b] and were especially close to those of $[(TE_{CHD})_2Cu^{III}{}_2O_2]^{2+}$ (TE_{CHD} = *N*,*N*,*N'*,*N'*-tetraethyl-1,2-cyclohexanediamine) in CH_2Cl_2 at –80 °C ($\nu(Cu_2(\mu\text{-}O)_2$ = 616/590 cm^{-1} ($^{16}O/^{18}O$))[2c], which substantiates formation of $[(Sp)_2Cu^{III}{}_2O_2]^{2+}$ (**4**) by the oxygenation of the solution of **3**. The two intense absorption bands of **4** in the UV region also indicated formation of a $Cu^{III}{}_2(\mu\text{-}O)_2$ core, whose intense band at 427 nm has been tentatively assigned as the oxo $\sigma_u{}^*$ to Cu $d_{x^2-y^2}$ CT transition band.[2d]

Table 1. Spectroscopic data of $Cu^{III}{}_2(\mu\text{-}O)_2$ complexes

Complex	LMCT band/nm (ε/$M^{-1}cm^{-1}(2Cu)^{-1}$) rR shift/cm^{-1} for $^{16}O_2/^{18}O_2$	Ref.
$[(Sp)_2Cu^{III}{}_2O_2]^{2+}$(**4**)	330 (12500), 427 (22800) 619/591	this work
$[(TM_{CHD})_2Cu^{III}{}_2O_2]^{2+}$	296 (20000), 392 (25000) 605/581	Ref. 2c
$[(ME_{CHD})_2Cu^{III}{}_2O_2]^{2+}$	306 (21000), 401 (28000) 610/587	Ref. 2c
$[(TE_{CHD})_2Cu^{III}{}_2O_2]^{2+}$	312 (17000), 406 (23000) 616/590	Ref. 2c
$[(Me3_{tacn})_2Cu^{III}{}_2O_2]^{2+}$	300 (12000), 405 (11000) 604/581	Ref. 2c
$[(Bn3_{tacn})_2Cu^{III}{}_2O_2]^{2+}$	318 (12000), 430 (14000) 602, 608/583	Ref. 2a

TM_{CHD} = *N*,*N*,*N'*,*N'*-tetramethyl-1,2-cyclohexanediamine, $Me3_{tacn}$ = 1,4,7-trimethyl-1,4,7-triazacyclononane

The absorption spectral features of **4**, however, are apparently distinct from those of the typical $Cu^{III}{}_2(\mu\text{-}O)_2$ complexes so far reported.[2] The two CT energies of **4** (330 nm and 427 nm) were significantly lower than those of the $Cu^{III}{}_2(\mu\text{-}O)_2$ complexes with peralkylated-1,2-cyclohexane-diamine (~312 nm and ~406 nm)[2c] (Table 1). This difference implies that the coordination geometry of the Cu(III) ion in **4** is distorted from the planar geometry as represented in the crystal structure of $[(ME_{CHD})_2Cu^{III}{}_2O_2](CF_3\text{–}SO_3)\cdot 4CH_2Cl_2$ (ME_{CHD} = *N*,*N'*-dimethyl-*N*,*N'*-diethyl-1,2-cyclohexanediamine).[2c] Although the spectral pattern of $Cu^{III}{}_2(\mu\text{-}O)_2$ complexes with 1,4,7-triazacyclononane derivatives are remarkably different from that of **4**,[2] $[(Bn3_{tacn})_2Cu^{III}{}_2O_2]^{2+}$ ($Bn3_{tacn}$ = 1,4,7-tribenzyl-1,4,7-triaza-cyclononane) exhibits two equally intense CT bands at relatively lower energy levels (λ_{max} = 318 and 430 nm (~ 14000)) (Table 1). The CT energies could be affected by a change from sqare planar to square pyramidal.[2d] The d-orbital splitting of the $Cu^{III}{}_2(\mu\text{-}O)_2$ core of **4** also appears to reflect its tetrahedral distortion of the planer core structure.

We are grateful to Professor Teizo Kitagawa, Institute for Molecular Science, for the use of the resonance Raman equipment. This work was supported by a Grant-in-Aid for Scientific Research (No. 09304062) from the Ministry of Education, Science, Sports, and Culture of Japan, for which we express our thanks.

References and Notes

1 a) N. Kitajima and Y. Moro-oka, *Chem. Rev.*, **94**, 737 (1994).

2 a) J. A. Halfen, S. Mahapatra, E. C. Wilkinson, S. Kaderli, V. G. Young Jr, L. Que, Jr., A. D. Zuberbühler, and W. B. Tolman, *Science*, **271**, 1397 (1996). b) P. L. Holland, C. J. Cramer, E. C. Wilkinson, S. Mahapatra, K. R. Rodgers, S. Itoh, M. Taki, S. Fukuzumi, L. Que, Jr., and W. B. Tolman, *J. Am. Chem. Soc.*, **122**, 792 (2000). c) V. Mahadevan, Z. Hou, A. P. Cole, D. E. Root, T. K. Lai, E. I. Solomon, and T. D. P. Stack, *J. Am. Chem. Soc.*, **119**, 11996 (1997). d) M. J. Henson, P. Mukherjee, D. E. Root, T. D. P. Stack, and E. I. Solomon, *J. Am. Chem. Soc.*, **121**, 10332 (1999).

3 a) S. Ito, H. Nakao, L. M. Berreau, T. Kondo, M. Komatsu, and S. Fukuzumi, *J. Am. Chem. Soc.*, **120**, 2890 (1998). b) H. Hayashi, S, Fujinami, S. Nagatomo, S. Ogo, M. Suzuki, A. Uehara, Y. Watanabe, and T. Kitagawa, *J. Am. Chem. Soc.*, **122**, 2124 (2000).

4 F. Binnig, *Arzeim.-Forsch.*, **24**,752 (1974).

5 a) L. S. Childers, K. Folting, L. L. Merritt, Jr., and W. E. Strieb, *Acta Cryst.*, **B31**, 924 (1975). b) R. Kuroda and S. F. Mason, *J. Chem. Soc., Dalton Trans.*, **1977**, 371. c) R. Kuroda, S. F. Mason, *J. Chem. Soc., Dalton Trans.*, **1979**, 727.

6 a) E. Boschmann, L. M. Weinstock, and M. Carmack, *Inorg. Chem.*, **13**, 1297 (1974). b) S. N. Choi, R. D. Bereman, and J. R. Wasson, *J. Inorg. Nucl. Chem.*, **37**, 2087 (1975).

7 Crystallographyic data for **1**: $CuC_{15}H_{26}N_2Cl_2$, fw = 368.84, orthorhombic ($P2_12_12_1$, a = 11.310(1) Å, b = 13.132(2) Å, c = 11.030(2) Å, V = 1638.0 $Å^3$), Z = 4, D_c = 1.496 g cm^{-3}, μ(Cu Kα) = 48.00 cm^{-1}, Independent reflections used ($\geq 3\sigma(|Fo|)$ 1451, R = 0.039, R_w = 0.057. Crystallographyic data for **2**: $Cu_2O_{10}C_{30}H_{52}N_4Cl_2$, fw = 824.74, monoclinic ($P2_1$, a = 10.131(2) Å, b = 14.834(3) Å, c = 12.085(2) Å, β = 99.90(1) °, V = 1789.2 $Å^3$), Z = 2, D_c = 1.531 g cm^{-3}, μ(Cu Kα) = 33.41 cm^{-1}, Independent reflections used ($\geq 3\sigma(|Fo|)$ 1777, R = 0.057, R_w = 0.076. A preliminary X-ray structure determination of **3** clearly confirmed that two nitrogen atoms of Sp and two CH_3CN coordinated to the Cu(I) ion in pseudo-terahedral geometry.