*Inorg. Chem.* **2001,** *40,* 4481−4484 **4481**

# A Mimic Molecule of Blue Copper Protein Active Site [(−)-Sparteine-*N,N′*](maleonitriledithiolato-*S,S′*)copper(II)

**Young-Jin Kim,[†] Su-Oak Kim, Young-Inn Kim, and Sung-Nak Choi***

Department of Chemistry and Department of Chemistry Education, Pusan National University, Pusan 609-735, Korea

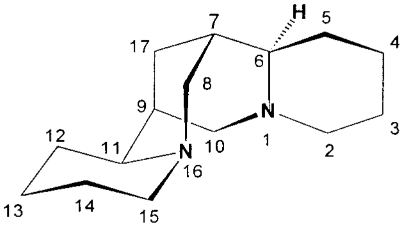
*Received December 11, 2000*

## Introduction

Considerable effort has been devoted to the design of model compounds and the elucidation of copper binding sites in metalloproteins.[1] A particularly intriguing example is the type 1 blue copper protein, which compared with tetragonal copper complexes exhibits intense absorption at ∼600 nm, distinctive electron spin resonance spectra, and unusually high redox potentials. These extraordinary properties are known to be related to the copper coordination sphere in the type 1 proteins.[1,2] A type 1 copper protein, such as plastocyanin, has a single Cu ion bonded in a distorted tetrahedral geometry to two imidazoles (histidine), one thiolate (cysteine), and one thioether (methionine).[3] Thus model studies on the blue copper proteins have mainly focused on the ligand donor systems containing thiolate, thioether, and thiocarboxylate groups, while imidazole binding is often simulated by imine groups or heterocyclic nitrogen bases.[1f,4]

Authentic synthesis and characterization of the tetrahedrally distorted Cu(II) compounds with the $Cu(II)S_2N_2$ chromophore would be invaluable for better understanding the detailed structural/electronic properties of the type 1 copper proteins, because a variety of "tetrahedral" geometries exist in their active sites.

Over the past three decades, several studies on copper(II) complexes of the neutral alkaloid (−)-sparteine (SP) have been reported.[5,6] The crystal structures of copper(II) sparteine complexes with chloride, nitrate, and acetate have been determined, and the copper(II) centers in these complexes are always found to have a distorted tetrahedral geometry.[6]



(-)Sparteine (6R, 11S)

In this study, we attempted to synthesize a new class of mimic model compounds for the type 1 copper site by introducing the maleonitriledithiolate, $C_4N_2S_2^{2-}$, into the copper(II) sparteine moiety. The synthesis of [(−)-sparteine-*N,N′*](maleonitrile-dithiolato-*S,S′*)copper(II), (SP)Cu(mnt), was prompted by our previous interest in the copper(II) sparteine complexes as potential models for distorted-tetrahedral environments of the type 1 copper(II) active sites.[7]

## Experimental Section

**Materials.** The (−)-sparteine ($C_{15}H_{26}N_2$, SP) was purchased from the Aldrich Chemical Co. All of the reagents were commercially received from Fisher and Fluka. All of the solvents were dried, distilled, and rigorously degassed before being used. The potassium salt of maleonitriledithiolate salt ($K_2$mnt) was prepared by methods previously reported in the literature.[8]

Tetrabutylammonium hexafluorophosphate, $Bu_4NPF_6$ (Fluka), used as a supporting electrolyte for electrochemical studies, was recrystallized twice from absolute ethanol and dried for 2 days at 110 °C prior to use. Anhydrous acetonitrile solvent was dried over molecular sieves (4A) and used for electrochemical studies. Bis(nitrato)[sparteine-*N,N′*]-copper(II), (SP)Cu($NO_3$)$_2$, was prepared according to the procedures previously described.[7]

**Preparation of [(−)-Sparteine-*N,N′*](maleonitriledithiolato-*S,S′*)-copper(II), (SP)Cu(mnt).** A degassed solution of potassium maleonitriledithiolate ($K_2$mnt: 0.218 g, 1.0 mmol) in 20 mL of methanol was slowly added to a solution of (SP)Cu($NO_3$)$_2$ (0.42 g, 1.0 mmol) in methylene chloride (30 mL), and the mixture was continuously stirred for 2 h at room temperature. An intensely dark greenish-blue solution was formed as a result. The solvent was slowly evaporated, and the resulting crude residue was dissolved in dry methylene chloride and then filtered. The filtrate was slowly evaporated, and then cold ethanol (30 mL) was added to the filtrate. The dark green solution was cooled overnight, and the resulting solid was collected by filtration, washed with cold ethanol, and dried in a vacuum. The solid was recrystallized from $CH_2Cl_2$/EtOH. Yield: 0.25 g (58%). IR (KBr): 2930 (s), 2866 (m), 2195 (s), 1466 (m), 1445 (s), 1151 (m), 1118 (m), 718 (w), 512

---

* To whom correspondence should be addressed. E-mail: sunachoi@hyowon.pusan.ac.kr. Tel: 82−51−510−2238. Fax: 82−51−516−7421.

[†] Current address: Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL. 60208. Tel: (847) 491-2435; Fax: (847) 491-7713.

(1) (a) Gray, H. B.; Solomon, E. I. In *Copper Protein*; Spiro, T. G., Ed.; Wiley: New York, 1981; pp 1−39. (b) Adman, E. T. *Adv. Protein Chem.* **1991**, *42*, 145−197. (c) Solomon, E. I.; Baldwin, M. J.; Lowery, M. D. *Chem. Rev.* **1992**, *92*, 521−542. (d) Pierloot, K.; De Kerpel, J. O. A.; Ryde, U.; Olsson, M. H. M.; Roos, B. O. *J. Am. Chem. Soc.* **1998**, *120*, 13156−13166. (e) Palmer, A. E.; Randall, D. W.; Xu, F.; Solomon, E. I. *J. Am. Chem. Soc.* **1999**, *121*, 7138−7149. (f) Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **2000**, *122*, 6331−6332.

(2) (a) Sykes, A. G. *Adv. Inorg. Chem.* **1991**, *36*, 377−408. (b) Adman, E. T. In *Topics in Molecular and Structural Biology: Metalloproteins*; Harrison, P., Ed.; MacMillan: New York, 1985; Vol 1 pp 1−42. (c) Hellinga, H. W. *J. Am. Chem. Soc.* **1998**, *120*, 10055−1006. (d) Holm, R. H.; Kennepohl, P.; Solomon, E. I. *Chem. Rev.* **1996**, *96*, 2239−2314.

(3) (a) Adman, E. T. *Curr. Opin. Struct. Biol.* **1991**, *1*, 895−904. (b) Colman, P. M.; Freeman, H. C.; Guss, J. M.; Murata, M.; Norris, V. A.; Ramshaw, J. A. M.; Venkatappa, M. P. *Nature* **1978**, *272*, 319−324. (c) Faham, S.; Mizoguchi, T. J.; Adman, E. T.; Gray, H. B.; Richards, J. H.; Rees, D. C. *J. Biol. Inorg. Chem.* **1997**, *2*, 464−469.

(4) (a) Anderson, O. P.; Perkins, C. M.; Brito, K. K. *Inorg. Chem.* **1983**, *22*, 1267−1273. (b) Sugiura, Y. *Inorg. Chem.* **1978**, *17*, 2176−2182.

(5) (a) Boschmann, E.; Weinstock, L. M.; Carmack, M. *Inorg. Chem.* **1974**, *13* 1297−1300. (b) Fraenkel, G.; Appleman, B.; Ray J. G. *J. Am. Chem. Soc.*, **1974**, *96*, 5113−5117. (c) Cady, W. A.; Boschman, E.; Choi, R. S.; Heidelman, J. F.; Smith, S. L. *Inorg. Chem.* **1977**, *16*, 1958−1961

(6) (a) Lopez, S.; Muravyov, L.; Pulley, S. R.; Keller, S. W. *Acta Crystallogr.* **1998**, *C54*, 355−357. (b) Childers, L. S.; Folding, K.; Meritt, Jro, Lo; Storeib, W. *Acta Cryst.* **1975**, *B31*, 924−925. (c) Lee, Y. M.; Chung, G.; Kwown, M. A.; Choi, S. N. *Acta Crystallogr.* **2000**, *C56*, 67−68. (d) Choi, S. N.; Kwon, M. A.; Kim, Y.; Bereman, R. D.; Singh, P.; Knight, B.; Seff, K. *J. Coord. Chem.* **1995**, *34*, 241−252.

(7) Choi, S. N.; Bereman, R. D.; Wasson, J. R. J. *Inorg. Nucl. Chem.* **1975**, *37*, 2087−2090.

(8) Simmons, H. E.; Vest, R. D.; Blomstrom, D. C.; Roland, J. R.; Cairns, T. L. *J. Am. Chem. Soc.* **1962**, *84*, 4746−4756.

10.1021/ic001396i CCC: $20.00

(w) cm$^{-1}$. Anal. Calcd for $C_{19}H_{26}N_4S_2Cu$: C, 52.08; H, 5.98; N, 12.79; S, 14.64. Found: C, 51.67; H, 6.10; N, 12.52; S, 14.43. The single crystal for X-ray diffraction was grown by slow diffusion in a cooling mixture of *n*-heptane/$CH_2Cl_2$.

**General Procedures.** All preparations were conducted using the Schlenk technique under a nitrogen atmosphere. The IR spectra (KBr pellets) were obtained by using the Bio-rad FTIR spectrophotometer over a range of 4000 ∼ 400 cm$^{-1}$. Electronic absorption spectra were obtained by using the HP 8452 A diode array spectrophotometer.

The CD spectra were obtained by using the Jasco J-700 spectropolarimeter (200−800 nm). Electrochemical experiments were performed under nitrogen by using a single-compartment cell with a platinum disk working electrode, an Ag/AgCl reference electrode, and a platinum wire counter electrode. Measurements were taken with a CH Instruments Model 9000 SECM at room temperature in the nitrogen-saturated acetonitrile solution containing ca. 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. EPR measurements were conducted with an ESP-300S Brucker spectrometer operating at X-band frequency (9.43 GHz). The external magnetic field was calibrated with a microwave bridge, a Model ER 032 MR Brucker wavemeter, and the temperature was controlled with a Model ER 4111 VT Brucker device with accuracy of ± 1%. Elemental analysis (C, H, N, and S) was performed at the Korea Research Institute of Standards and Science.

**X-ray Crystallography.** A blue plate crystal of (SP)Cu(mnt) was cut from a larger crystal, and the resulting crystal having dimensions of approximately 0.04 × 0.14 × 0.17 mm was mounted by using oil (Paratone-N, Exxon) on a glass fiber. All the measurements were made on a SMART-1000 CCD area detector with graphite monochromated Mo Kα ($\lambda$ = 0.71069 Å) radiation. The data were collected at a temperature of $-120 \pm 1$ °C, to a maximum $2\theta$ value of 56.6°. Data were collected in 0.30° oscillations with 25.0 s exposures. The crystal−to−detector distance was 50.00 mm. The detector swing angle was 28.00°. Of the 26,754 reflections collected, 6,330 were unique ($R_{\mathrm{int}}$ = 0.122); equivalent reflections were merged. Data were collected and processed by using the SMART-NT and SAINT-NT programs (Bruker).

The linear absorption coefficient, $\mu$, for Mo Kα radiation was 13.5 cm$^{-1}$. An empirical absorption correction was applied. Maximum and minimum effective transmission factors were 1.000000 and 0.302731, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by the direct method (SIR92)[9] and expanded by using the Fourier techniques.[10] The present full-matrix least-squares refinement for $\sum w(F_o^2 - F_c^2)^2$ on $F^2$ was based on a total of 3,222 observed reflections with 139 variable parameters and were converged with unweighted and weighted agreement factors of $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.069$ and $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2} = 0.127$. The standard deviation of an observation of unit weight $[\sum w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$ (where $N_o$ is number of observations and $N_v$ is the number of variables) was 1.93. The weighting scheme was based on the counting statistics plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map were 1.41 and −1.18 e$^-$/Å$^3$, respectively, and the peaks were in the vicinity of the Cu position. Data collection and appropriate refinement parameters are summarized in the Supporting Information. All of the calculations were performed by using the teXsan crystallographic software package Molecular Structure Corporation.

## Results and Discussion

We recently reported the synthesis and structure of both four- and five-coordinate Cu(II) complexes by introducing the highly steric hindered (−)-sparteine as a supporting ligand.[5] The bulky fused rings of the sparteine ligand induce a pseudo-tetrahedral environment around the copper(II) center of the four-coordinate complexes.

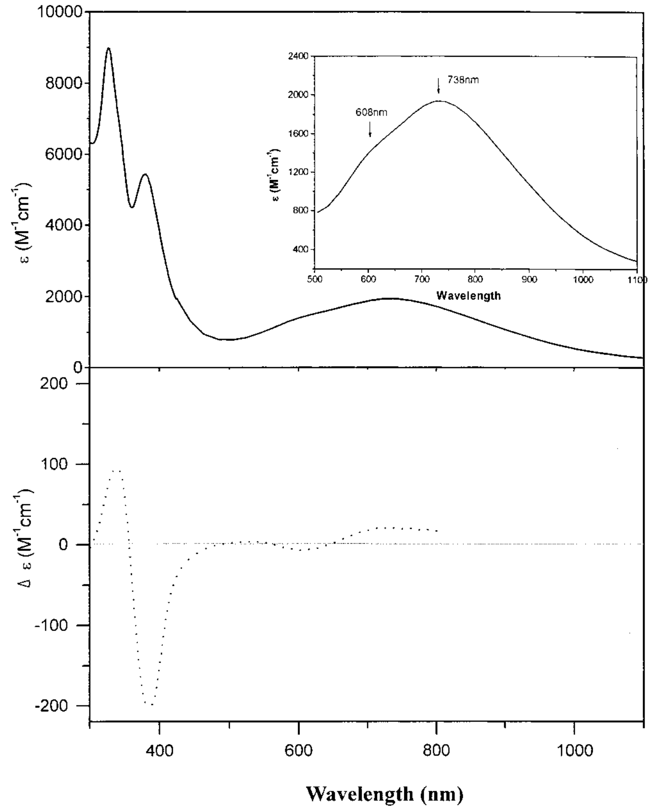


**Figure 1.** (a) UV−Visible and (b) CD spectra of the (SP)Cu(mnt) complex in degassed methylene chloride solution.

Most copper(II) sparteine complexes could be obtained from the precursor complex, (SP)Cu($NO_3$)$_2$, because the nitrate ligand in this compound is very labile and easily undergoes ligand exchanges with various anions.[6]

In this study, solutions of (SP)Cu($NO_3$)$_2$ in $CH_2Cl_2$/MeOH (3:1) mixture were treated with the potassium salt of maleonitriledithiolate ($K_2$mnt) to obtain the corresponding neutral (SP)Cu(mnt) complex. The product was isolated as a stable dark blue solid. This product is an unusual example of a mixed ligand metal complex with tertiary diamine and dithiolate ligands on the central metal ion, and it was characterized by UV−vis, IR, and elemental analyses. Slow diffusion of *n*-heptane into a methylene chloride solution of (SP)Cu(mnt) in a freezer yielded dark blue crystals suitable for our X-ray crystallographic studies.

Substituting the nitrate group with the dithiolate group resulted in expected changes: an appearance of the characteristic CN stretching band of maleonitriledithiolate at 2195 cm$^{-1}$, and the disappearance of the characteristic bands of the nitrate group occurring at 1384, 1282, and 1273 cm$^{-1}$ in the (SP)Cu($NO_3$)$_2$ complex.

Figure 1 shows the electronic absorption and the CD spectra of the (SP)Cu(mnt) complex in $CH_2Cl_2$. A broad and intense absorption envelope in the region of 500−1000 nm is asymmetrical. The intense band at 738 nm and the shoulder band at ∼608 nm are assinged to S→ Cu(II) charge transfer(CT) bands.

These intense CT bands are unique for (SP)Cu(mnt). Other similar metal complexes, such as (SP)Zn(mmt), (SP)Co(mmt), and (SP)CuCl$_2$, do not exhibit any intense bands ($\epsilon$ =1000 M$^{-1}$ cm$^{-1}$) in the region of 600 ∼ 800 nm (Table S1, and Figures S1 and S2), and the maleonitriledithiolate ligand does not show any absorption bands in the same region. Thus, these two intense bands of (SP)Cu(mnt) are not originated either from the ligand field (LF) transtion or the intraligand transtion. The CD spectra of (SP)Cu(mnt) exhibits two bands at 604 nm ($\Delta\epsilon$ = −12.50

---

(9) SIR 92: Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Cryst.* **1993**, *26*, 343−350.

(10) DIRDIF 94: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.

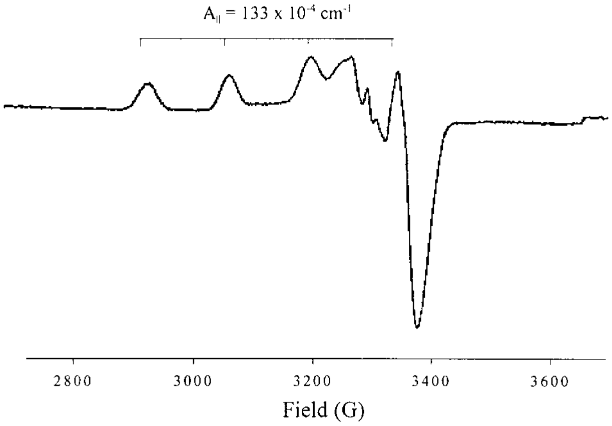


**Figure 2.** X-Band EPR spectrum of the (SP)Cu(mnt) complex in methylene chloride/toluene (1:1) at 77 K.

$M^{-1}$ $cm^{-1}$) and 745 nm ($\Delta\epsilon = +21.0$ $M^{-1}$ $cm^{-1}$), supporting that two S→ Cu(II) transtions occur in this compound.

Only one LF band of (SP)Cu(mnt) is observed at 1405 nm ($\epsilon = 151$ $M^{-1}$ $cm^{-1}$), but other expected LF bands have not been observed. These unobserved bands may lie close to the intense CT bands at 738 nm and contribute to a possible intensity enhancement of the CT band. However, the intensities of LF bands of (SP)Cu(mnt) and (SP)$CuCl_2$ are ~200 $M^{-1}$ $cm^{-1}$ or less, indicating that the intensity enhancement of CT bands by the LF bands may not be substaintial.

The electronic absorption spectrum of (SP)Cu(mnt) in this region strongly resembles the intense S → Cu(II) LMCT band of the type 1 copper protein. The charge-transfer spectral feature of (SP)Cu(mnt) is also quite similar to that of the $\beta$-diketimine copper(II) complex having a tetrahedrally distorted $CuN_2S$-(thiolate)S(thioether) chromophore, as reported by Tollman et al.[1f] The LMCT band of copper(II) thiolate systems is often observed in the higher energy region.[11] The LMCT band centered at 738 nm for (SP)Cu(mnt) is one of the lowest energy transition bands observed for small copper(II) model compounds with the same donor set as the type 1 copper protein active center.

Figure 2 shows the X-band EPR spectrum of the (SP)Cu-(mnt) complex at 77 K in $CH_2Cl_2$/toluene (1:1) frozen glass, where $g_{\|} = 2.16$ and $A_{\|} = 133 \times 10^{-4}$ $cm^{-1}$ were evaluated. In addition, the signal for (SP)Cu(mnt) is rhombic, where the $g_{\perp}$ value splits into $g_x = 2.00$ and $g_y = 2.06$. The tetrahedral distortion from the planar $Cu^{II}S_4$ moiety simultaneously decreases the $A_{\|}$ value and increases the $g_{\|}$ value.[12] In fact, the $g_{\|}$ value of $Cu^{II}S_4$, as well as that of $Cu^{II}N_4$ complexes, tends to increase as the $A_{\|}$ value decreases. Such tendency, however, is vague in the $Cu^{II}N_2S_2$ systems.[13] Although the $A_{\|}$ value of (SP)-Cu(mnt) is larger by a factor of 2 ~ 3 than values reported for the native type copper sites, this value is significantly smaller than those of other $Cu^{II}N_2S_2$ complexes with amino- or pyridyl-nitrogen donors and thioether sulfur donors as ligating atoms ($A_{\|} = 175 \times 10^{-4}$ $cm^{-1}$).[9,14] On this basis, the reduced $A_{\|}$ value of $133 \times 10^{-4}$ $cm^{-1}$ for (SP)Cu(mnt) is attributable to a distinct distortion of a square-planar configuration of the $Cu^{II}N_2S_2$ framework toward a tetrahedral geometry.

An ORTEP diagram of the (SP)Cu(mnt) complex is shown in Figure 3. The $Cu^{II}-S$ and the $Cu^{II}-N$ bond lengths in (SP)-Cu(mnt) are ~2.2 and ~2.0 Å, respectively.

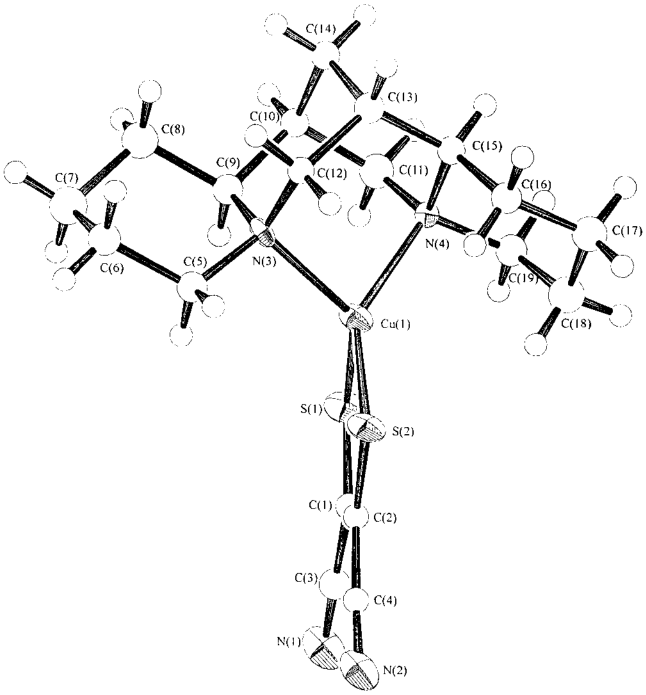


**Figure 3.** ORTEP diagram of (SP)Cu(mnt). The thermal ellipsoids shown in the figure are at the 50% probability levels.

The $Cu^{II}-S$ bond in this model compound is 0.1 Å longer than the $Cu^{II}-S$ (cysteine) bond and 0.6 Å shorter than the $Cu^{II}-S$ (methionine) bond in the blue copper protein. Two typical Cu−N bond lengths around 2.0 Å were established previously by EXAFS studies for the "blue" copper site.[15] The S(1)−Cu−S(2) bond angle is 94.47° and is smaller for (SP)-Cu(mnt) than for plastocyanin (107°).[16]

In addition, the (SP)Cu(mnt) complex shows an expected overall geometric feature, with the sparteine molecule acting as a bidentate ligand in its chair conformation. The N(3)−Cu−N(4) bond angle of 89.1° (less than 90°) is a result of the steric requirement of the rigid bidentate diamine ligand. The Cu atom adopts a distorted tetrahedral geometry, with a dihedral angle of 68.07° between the $N_2Cu$ and the $S_2Cu$ planes, and the overall geometry of (SP)Cu(mnt) is shown to be partially consistent with that of type 1 copper sites with low and probably distorted tetrahedral symmetries.[17] The crystallographic data and selected bond parameters are summarized in Tables 1 and 2.

Perhaps most interestingly, the cyclic voltammogram of (SP)-Cu(mmt) produces a quasi-reversible wave with a very positive cathodic peak potential ($E_{pc} = +0.300$ V versus Ag/AgCl), which is due to the electrode reaction: (SP)Cu(mnt) + $e^-$ → $[(SP)Cu(mnt)]^-$.

The reaction is also slightly irreversible chemically ($i_{pa}/i_{pc} = 0.47$; $\Delta E_p = 106$ mV), and this reduction potential value is far

---

(11) (a) Anderson, O. P.; Perkins, C. M.; Brito, K. K. *Inorg. Chem.* **1983**, *22*, 1267−1273. (b) Amundsen, A. M.; Whelan, J.; Bosnich, B. *Inorg. Chem.* **1979**, *18*, 206−208.

(12) Cannas, M.; Carta, G.; Marongiu, G. *J. Chem. Soc., Dalton Trans.* **1974**, 556−558.

(13) Sakaguchi, U.; Addison, A. W. *J. Chem. Soc., Dalton Trans.* **1979**, 600−608.

(14) Fawcett, T. G.; Bernaducci, E. E.; Krogh-Jespersen, K.; Schugar, H. J. *J. Am. Chem. Soc.* **1980**, *102*, 2598−2604.

(15) Guss, J. M.; Bartunik, H. D.; Freeman, H. C. *Acta Crystallogr.* **1992**, *B48*, 790−811.

(16) Guss, J. M.; Freeman, H. C. *J. Mol. Biol.* **1983**, *169*, 521−563.

(17) (a) Xu, F.; Shin, W.; Brown, S. H.; Wahleithner, J. A.; Sundaram, U. M.; Solomon, E. I. *Biochim. Biophys. Acta* **1996**, *1292*, 303−311. (b) Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143−207. (c) Iwata, S.; Ostermeier, C.; Ludwig, B.; Michel, H. *Nature* **1995**, *376*, 660−669. (d) Wilmanns, M.; Lappalainen, P.; Kelly, M.; Sauer-Ericksson, E.; Saraste, M. *Proc. Natl. Acad. Sci. U.S.A.* **1995**, *92*, 11955−11959.

**Table 1.** Crystal Data and Structure Refinement for (Sp)Cu(mnt)

| | |
|---|---|
| empirical formula | $C_{19}H_{26}N_4S_2Cu$ |
| fw | 438.11 |
| temp | 153(1) K |
| cryst syst | hexagonal |
| space group | $P6_1$(No.169) |
| *a* | 8.569(3) Å |
| *c* | 45.78(2) |
| *Z* | 6 |
| $d_{cal}$ | 1.499 g/cm$^3$ |
| *F*(000) | 1374.00 |
| reflns collected/unique | 26754/6330 [R(int) = 0.122] |
| GOF indicator | 1.93 |
| final R indices [$I > 2\sigma(I)$] | $R_1 = 0.069^a$, $wR_2 = 0.127^b$ |

$^a$ $R_1 = ||F_o| - |F_c||/|F_o|$. $^b wR_2 = [w(F_o^2 - F_c^2)^2/w(F_o^2)^2]^{1/2}$.

**Table 2.** Selected Bond Parameters for (SP)Cu(mnt)

Distances (Å)

| atom | atom | distance | atom | atom | distance |
|---|---|---|---|---|---|
| Cu1 | S1 | 2.266(3) | Cu1 | S2 | 2.239(3) |
| Cu1 | N3 | 2.027(8) | Cu1 | N4 | 2.036(8) |
| S1 | C1 | 1.715(10) | S2 | C2 | 1.736(10) |
| N1 | C3 | 1.159(13) | N2 | C4 | 1.186(12) |
| N3 | C5 | 1.484(13) | N3 | C9 | 1.459(12) |
| N3 | C12 | 1.489(12) | N4 | C11 | 1.422(12) |
| N4 | C15 | 1.548(12) | N4 | C19 | 1.520(12) |

Angles (Deg)

| atom | atom | atom | angle | atom | atom | atom | angle |
|---|---|---|---|---|---|---|---|
| S1 | Cu1 | S2 | 94.47(12) | S1 | Cu1 | N3 | 125.4(3) |
| S1 | Cu1 | N4 | 102.8(2) | S2 | Cu1 | N3 | 109.5(2) |
| S2 | Cu1 | N4 | 140.4(2) | N3 | Cu1 | N4 | 89.1(3) |
| Cu1 | S1 | C1 | 98.0(4) | Cu1 | S2 | C2 | 99.4(4) |
| Cu1 | N3 | C5 | 105.7(6) | Cu1 | N3 | C9 | 107.2(6) |
| Cu1 | N3 | C12 | 108.9(6) | C5 | N3 | C9 | 109.3(8) |
| C5 | N3 | C12 | 110.6(8) | C9 | N3 | C12 | 114.6(8) |
| Cu1 | N4 | C11 | 108.3(6) | Cu1 | N4 | C15 | 110.6(6) |
| Cu1 | N4 | C19 | 108.3(6) | C11 | N4 | C15 | 111.3(8) |

more positive than those of the corresponding copper(II) sparteine complexes.[18] The minor stereochemical reorganization on one-electron reduction and the presence of soft sulfur atoms might combine to make the redox potential of the Cu(II)/Cu(I) couple of (SP)Cu(mnt) rather high, as was suggested in the case of plastocyanin.[19] However, the more positive reduction potential value of (SP)Cu(mnt) is attributable mainly to the presence of two sulfur donors, which can stabilize the +1 oxidation state of copper. The site symmetries around copper(II) in (SP)Cu(mnt) and in [sparteine *N*,*N'*]dichlorocopper(II), (SP)$CuCl_2$, are quite similar. The dihedral angle between the $N_2Cu$ and the $Cl_2Cu$ planes is 67.0° for (SP)$CuCl_2$,[6a] and this angle is very similar to the dihedral angle between the $N_2Cu$ and the $S_2Cu$ planes in (SP)Cu(mnt) (68.07 °). However, the difference in the cathodic peak potential value between (SP)Cu(mnt) and (SP)$CuCl_2$ is still substantial (~0.5 V).

In conclusion, this study showed that the (−)-sparteine and the maleonitriledithiolate ligands can provide useful nitrogen and sulfur donors to form stable and tetrahedrally distorted copper(II)(nitrogen)$_2$(sulfur)$_2$ complexes of mixed ligand systems. Although the present ligands do not accurately represent active site of the blue copper(II) proteins, the heterocyclic tertiary amine group as nitrogen donors and the dithiolate group as sulfur donors may produce copper(II) model complexes that closely mimic interesting spectral and redox behaviors in the blue copper centers.

**Acknowledgment.** The financial support of the Korean Science and Engineering Foundation (Grant No. 2000-1-12200-005-1) is gratefully acknowledged. We thank Charlotte L. Stern for collecting the X-ray data for the title compound.

**Supporting Information Available:** Cyclic voltammogram, tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, anisotropic thermal parameters for (SP)Cu(mnt), and an X-ray crystallographic file (CIF format) for (SP)Cu(mnt). This material is available free of charge via the Internet at http://pubs.acs.org.

IC001396I

---

(18) For (SP)$CuCl_2$, (SP)$CuBr_2$, and (SP)Cu($NO_3$)$Br_2$, $E_{pc} = -0.220$, $-0.050$, and $-0.105$ V (versus Ag/AgCl), respectively. Kim, Y. and Choi, S.-N., unpublished results. The cyclicvoltametric data of these compounds are summarized in Table S2 and Figure S3.

(19) Guss, J. M.; Harrowell, P. R.; Murata, M.; Norris, V. A.; Freeman, H. C. *J. Mol. Biol.* **1986**, *192*, 361−387.