# Preparation and Characterization of Macrocyclic Tetraamine Dimethylthiolate Copper(II) Complex

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A novel compound, $[Cu(L)(SCH_3)_2]\cdot 2H_2O$ **1** ( L = 3, 14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,$0^{1.18}$,$0^{7.12}$]docosane), bridged by two thiolate sulfur atoms, has been prepared and characterized. The copper(II) ion adopts a tetragonally elongated octahedral geometry with two axial thiolate sulfur atoms.

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The thiolate complexes of copper(II) are of interest in relation to the active site of blue copper proteins such as azurin[1] and plastocyanion.[2] However, structurally characterized mononuclear copper(II)-thiolate complexes are limited to a few examples with aromatic[3-6] and aliphatic thiolates,[7,8] because of the thermodynamic instability of such complexes, which lead to the reduction of the metal to copper(I) and formation of the appropriate disulfide.[9] With $NaSCH_3$, however, most stable complex $[Cu(L)(SCH_3)_2]\cdot 2H_2O$ **1** (L= 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,$0^{1.18}$,$0^{7.12}$]docosae) was successfully obtained, and the complex was isolated and crystallized. In this communication, we describe the preparation and crystal structure of a thiolato complex **1**.

To a methanol (20 ml) solution of $[Cu(L)]Cl_2\cdot 2H_2O$ **2**[10] (200 mg, 0.39 mmol) was added $NaSCH_3$ (55 mg, 0.78 mmol) and the mixture refluxed for 1hr. The solution was then taken to dryness, and the resulting solid dissolved in acetonitrile/water (1:1, 10 ml) solvent mixture. When this mixture was allowed to stand for a few days, X-ray quality crystals formed. These were collected with filtration, washed with a small amount of diethyl ether, and dried in vacuo (yield 110 mg, 53%).[11] The structure of $[Cu(L)(SCH_3)_2]\cdot 2H_2O$ **1**, determined by X-ray crystallographic analysis,[12] together with the atom labelling scheme is shown in Figure 1.

The structure of complex **1** contains a copper atom facially coordinated $N_4$ macrocycle with two thiolate sulfur atoms. The average Cu-N distance of 2.020 Å and the N-Cu-N angles of the six-membered chelate rings of **1** are larger than those of the five-membered chelate rings. The methyl group on a six-membered chelate ring is anti with respect to the $N_4$ plane. The axial Cu-S linkages are bent slightly off the perpendicular to the $CuN_4$ plane by 1-8 °. The CuSC angle of 176.9(2)° is larger in comparison with the other o-mercaptobenzonate(108.4(4)° ).[3] The axial Cu-S bond distance of 2.659(1) is at the middle of the range (2.56-2.82 Å) expected for axial Cu-S bonds.[13] To our knowledge, a small number of four-, five- and six-coordinate structures containing a mixture of nitrogen and sulfur donors have been previously characterized by X-ray crystallography. Kitajima et al.[6] reported a distorted tetrahedral or trigonal pyramidal complex $[Cu(SC_6F_5)(HB(3,5\text{-}i\mathrm{Pr}_2pz)_3)]$ in which the copper (II)-thiolate sulfur distance of 2.176 Å is remarkably short due to the basal position of thiolate sulfur donor atom. On the other hand, the axial Cu-S bond distances of $[Cu(L)](ClO_4)_2$ ( L = 15-thia-1,5,8,12-tetraazabicyclo [10.5.2]nonadecane) and $[Cu([9]\text{-aneSN}_2)Br_2]$ which have both five-coordinate square pyramidal complexes are 2.549[14] and 2.567 Å,[15] respectively. In contrast, the Cu-S bonds in the octahedral $[Cu([9]\text{-aneSN}_2)_2]^{2+}$ are considerably longer (2.707 Å)[16] due to a coordination number of six, resulting in elongation of both axial bonds. This complex has axial Cu-S distance resembling the distance found in the present complex **1**. Thus, Cu-S value of 2.659(1) Å appears appropriate for the axially elongated bonds in octahedral copper(II) complex. The

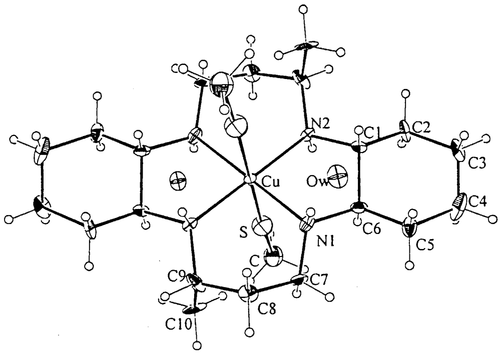

**Figure 1.** ORTEP drawing of **1** showing the atomic labelling scheme. Selected bond distances(Å) and angles (° ): Cu-S 2.659(1), Cu-N(1) 2.013(3), Cu-N(2) 2.027(3), S-C 1.828(3), N(1)-Cu-S 89.2(1), N(2)-Cu-S 97.6(1), N(1)-Cu-N(2) 86.7(1), C-S-Cu 176.9(2).

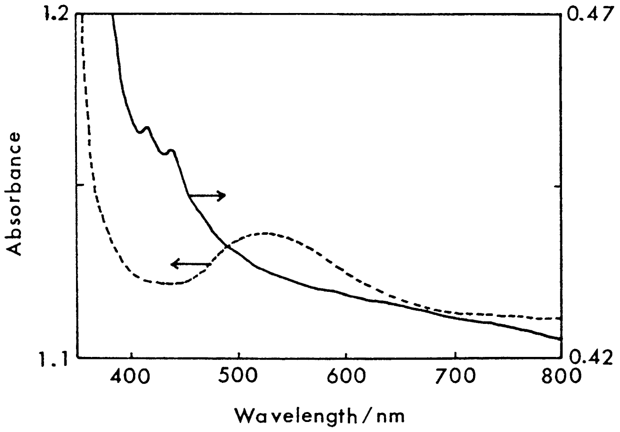

**Figure 2.** Electronic absorption spectra of **1** (—) and **2** ( - - - ) in a Nujol mull at 25 ℃.

thiolate sulfur atom forms two hydrogen bonding OW···S(3.127(4) Å) and $OW^i$···S( -x, 1-y, -1-z, 3.133(3) Å) of adjacent complex **1**. As in the solid state structure of **2**[10], **1** also adopts a thermodynamically most stable trans-Ⅲ conformations in the solid state.

The solid-state spectrum of **1** in Figure 2 appears the absorptions at 416 and 435 nm, which may be assigned to the sulfur-to-copper(Ⅱ) charge transfer transitions, since the complex **2** exhibits no absorption bonds in that region. This result is similar to that of found in [Cu(tet b)(o-$SC_6H_4CO_2$)] · $H_2O$.[3]

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## References and Notes

1 G. E. Norris, B. F. Anderson, and E. N. Baker, *J. Am. Chem. Soc.*, **108**, 2784 (1986).
2 J. M. Guss, P. R. Harrowell, M. Murata, V. A. Norris, and H. C. Freeman, *J. Mol. Biol.*, **192**, 361 (1986).
3 J. L. Hughey, T. G. Fawcett, S. M. Rudich, R. A. Lalancette, J. A. Potenza, and H. J. Schugar, *J. Am. Chem. Soc.*, **101**, 2617 (1979).
4 A. W. Addison and E. Sinn, *Inorg. Chem.*, **22**, 1225 (1983).
5 N. Aoi, Y. Takano, H. Ogino, G. Matsubayashi, and T. Tanaka, *J. Chem. Soc., Chem. Commun.*, **1985**, 703.
6 N. Kitajima, K. Fujisawa, M. Tanaka, and Y. Moro-oka, *J. Am. Chem. Soc.*, **114**, 9232 (1992).
7 E. John, P. K. Bharadwaj, J. A. Potenza, and H. J. Schugar, *Inorg. Chem.*, **25**, 3065 (1986).
8 P. K. Bharadwaj, J. A. Potenza, and H. J. Schugar, *J. Am. Chem. Soc.*, **108**, 1351 (1986).
9 J. Whelan and B. Bosnich, *Inorg. Chem.*, **25**, 3671 (1986).
10 K.-Y. Choi, J. C. Kim, W. P. Jensen, I.-H. Suh, and S.-S. Choi, *Acta Crystallogr.*, **C52**, 2166 (1996).
11 FAB MS: m/z 401 $(M-2SCH_3 +H)^+$ IR (KBr) 3133 $(\nu_{NH})cm^{-1}$ ; UV/vis $\lambda_{max}$(Nujol) 416, 435 nm; Anal. Found: C, 49.67 ; H, 9.58 ; N, 10.51%. Calcd for $CuC_{22}H_{50}N_4O_2S_2$: C, 49.82 ; H, 9,50 ; N, 10.57%.
12 Crystal data for **1**: $CuC_{22}H_{50}N_4O_2S_2$, M = 530.33, monoclinic, space group $P2_1/c$, a = 9.016(1), b = 18.143(1), c = 7.866(1) Å, $\beta$ = 109.89(1)° , V = 1209.9(2) $Å^3$, Z = 2, $D_c$ = 1.40 $gcm^{-3}$, crystal size 0.2×0.2×0.2 $mm^3$, $\lambda(MoK\alpha)$= 0.71069 Å, $\mu$ = 1.09 $mm^{-1}$, 1810 data collected at 288 K on an Enraf-Nonius CAD-4 diffractometer. The structure was solved by the heavy atom method and refined anisotropically by using a total of 1351 reflections $[|F_o| > 4\sigma(|F_o|)]$ to give R = 0.0263 and Rw = 0.0795. The program used was NRCVAX PC software package[17] and SHELXL93.[18]
13 J. C. A. Boyens, S. M. Dobson, and R. D Hancock, *Inorg. Chem.*, **24**, 3073 (1985).
14 D. G. Fortier and A. McAuley, *Inorg. Chem.*, **28**, 655 (1989).
15 R. D. Hancock, S. M. Dobson, and J. C. D. Boyens, *Inorg. Chim. Acta*, **133**, 221 (1987).
16 J. C. A. Boyens, S. M. Dobson, and R. D. Hancock, *Inorg., Chem.*, **24**, 3073 (1985).
17 E. J. Gabe, Y. L. Page, J. P. Charland, F. L. Lee, and P. S. White, An Interactive Program System for Structure Analysis, *J. Appl. Crystallogr.*, **22**, 384 (1989).
18 G. M. Scheldrick, A Program for Refinement of Crystal Structure, University of Gottingen, Germany (1993).