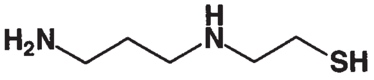
Thiolato-Bridged Hexanuclear $\mathrm{Cu^{I}Cu^{II}}$ Mixed-Valence Complex

Takanori Kotera and Masahiro Mikuriya*
Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, Sanda 669-1337

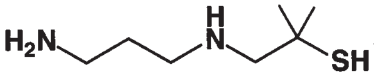
(Received March 28, 2002; CL-020281)

Thiolato-bridged hexanuclear mixed-valence complex, $[\mathrm{Cu^{I}_3Cu^{II}_3(apampt)_3Cl_6}]$ (Hapampt = 1-[(3-aminopropyl)amino]-2-methylpropane-2-thiol), has been synthesized and characterized by X-ray crystallography. Spectroscopic data as well as structural features support a localized mixed-valence state. Magnetic susceptibility data show that a strong antiferromagnetic interaction is operating between the $\mathrm{Cu^{II}}$ ions.

Metal-thiolate compounds are of considerable interest in relation to biologically significant metal-cysteine centers in metal enzymes.[1] Especially, thiolato-bridged $\mathrm{Cu^{I}Cu^{II}}$ mixed-valence complexes have been focused from a view of models for nitrous oxide reductase and cytochrome *c* oxidase.[2] We have engaged in synthetic work on thiolato-bridged metal complexes with *N*, *N*, *S*-donor tridentate ligands with a view to developing the fundamental chemistry of metal thiolate compounds. So far, we isolated dinuclear,[3] trinuclear,[4,5] tetranuclear,[6] and infinite polynuclear[5] complexes of various metal ions except for copper ion by the use of these tridentate ligands including 2-[(3-aminopropyl)amino]ethanethiol (Hapaet). As part of this effort, we have synthesized a new *N*, *N*, *S*-donor tridentate thiolic ligand, 1-[(3-aminopropyl)amino]-2-methylpropane-2-thiol (Hapampt),[7] which has two methyl groups added in alpha position of the thiolato-sulfur, in attempt to extend our systems to copper chemistry and isolated a novel hexanuclear $\mathrm{Cu^{I}Cu^{II}}$ mixed-valence complex, $[\mathrm{Cu^{I}_3Cu^{II}_3(apampt)_3Cl_6}]$ (**1**). Herein we report synthesis and characterization of **1**.



Hapaet



Hapampt

Complex **1** was prepared as follows.[8] To a methanol (5 cm^3) solution of Hapampt (32 mg, 0.2 mmol) was added a methanol (5 cm^3) solution of copper (II) chloride dihydrate (34 mg, 0.2 mmol). The solution was stirred at ca. 25 °C for 5 min and filtered. The resulting light brown filtrate was allowed to stand several days at room temperature. Dark brown crystals deposited were collected by filtration. Yield, 27 mg (74% based on the metal source). Found: C, 22.56; H, 4.77; N,7.41%. Calcd for $\mathrm{C_{21}H_{55}Cl_6Cu_6N_6O_2S_3}$ C, 22.64; H, 4.98; N, 7.54%.

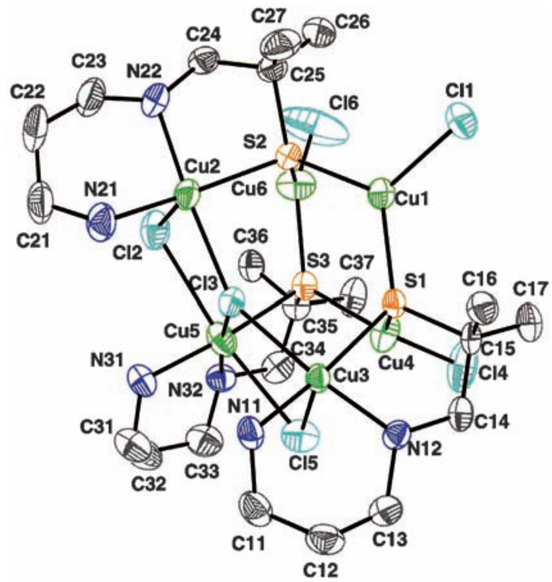


Figure 1. Perspective view of **1**·$2\mathrm{CH_3OH}$, showing the atom-labeling scheme. Solvent molecules and hydrogen atoms are omitted for clarity. Selected bond distances (l/Å) and angles (ϕ/°): Cu1–Cu2 3.958(1), Cu1–Cu3 3.925(1), Cu1–Cu4 3.722(1), Cu1–Cu5 5.229(2), Cu1–Cu6 3.521(2), Cu2–Cu3 4.625(1), Cu2–Cu4 5.420(2), Cu2–Cu5 3.850(1), Cu2–Cu6 3.506(2), Cu3–Cu4 3.375(1), Cu3–Cu5 3.872(2), Cu3–Cu6 5.396(2), Cu4–Cu5 3.547(2), Cu4–Cu6 3.777(2), Cu5–Cu6 3.730(2), Cu1–Cl1 2.226(2), Cu1–S1 2.226(2), Cu1–S2 2.225(2), Cu2–Cl2 2.607(2), Cu2–Cl3 2.370(2), Cu2–S2 2.273(2), Cu2–N21 2.005(6), Cu2–N22 2.019(6), Cu3–Cl3 2.396(2), Cu3–Cl5 2.557(2), Cu3–S1 2.271(2), Cu3–N11 1.990(5), Cu3–N12 2.022(5), Cu4–Cl4 2.238(2), Cu4–S1 2.259(2), Cu4–S3 2.237(2), Cu5–Cl2 2.762(2), Cu5–Cl3 2.696(2), Cu5–Cl5 2.839(2), Cu5–S3 2.253(2), Cu5–N31 1.979(5), Cu5–N32 2.051(5), Cu6–Cl6 2.216(3), Cu6–S2 2.230(2), Cu6–S3 2.232(2); Cu1–S1–Cu3 121.56(8), Cu1–S1–Cu4 112.16(8), Cu1–S2–Cu2 123.23(8), Cu1–S2–Cu6 104.44(8), Cu4–S3–Cu5 104.32(8), Cu4–S3–Cu6 115.34(8), Cu5–S3–Cu6 112.53(8), Cu2–Cl2–Cu5 91.57(7), Cu2–Cl3–Cu3 152.07(9), Cu3–Cl3–Cu5 98.82(7), Cu3–Cl5–Cu5 91.55(7).

The molecular structure of **1**·$2\mathrm{CH_3OH}$, which was determined by X-ray crystallography,[9] is shown in Figure 1. The hexanuclear copper core is composed of one six-membered ring [Cu1–S1–Cu4–S3–Cu6–S2] and two adjacent four-membered rings [Cu2–Cl3–Cu5–Cl2] and [Cu3–Cl5–Cu5–Cl3]. Charge consideration requires a formal $\mathrm{Cu^{I}_3Cu^{II}_3}$ description of this core and thus we can assign the Cu1, Cu4, and Cu6 atoms to $\mathrm{Cu^{I}}$ and the Cu2, Cu3, and Cu5 atoms to $\mathrm{Cu^{II}}$, respectively, based on the different coordination environments as described below. Each copper atoms (Cu1, Cu4, and Cu6) of the former chair-like ring is coordinated to two thiolato-sulfur atoms and chloride ion to form a trigonal planar geometry. The $\mathrm{Cu^{I}}$–S bond distances are 2.225(2)–2.259(2) Å. These bond lengths are within the range found in $\mathrm{Cu^{I}}$ complexes.[10] On the other hand, each of the three copper atoms (Cu2, Cu3, and Cu5) of the latter rings is chelated by thiolate ligand, $\mathrm{apampt^{-}}$, with *N*, *N*, *S*-donor atoms. Coordination environments of Cu2 and Cu3 can be described as an elongated square-pyramidal configuration with two amino-nitrogen atoms and thiolato-sulfur atoms (N21, N22, S2 for Cu2; N11, N12, S1 for Cu3) of apampt and chloride ion (Cl3) in the equatorial positions and a chloride ion (Cl2 for Cu2; Cl5 for Cu3) at the apex, while Cu5 takes a distorted octahedral geometry with two amino-nitrogen atoms and thiolato-sulfur atom of apampt (N31, N32, and S3) and three chloride ions (Cl2, Cl3, and Cl5). The Cu^{II}–S distances are 2.225(2)–2.273(2) Å. Interestingly, large difference is not found in these Cu^{II}–S distances compared with the Cu^{I}–S bonds. Ligation of thiolato-sulfur to copper (II) has been hardly established by synthesizing complexes, although such bonding is frequently observed in copper proteins. Both the Cu^{I}–S and Cu^{II}–S distances of the present complex are comparable to the values found in very few thiolato-bridged $Cu^{I}Cu^{II}$ mixed valence complexes.[2,11] The Cu–Cl bond distances around the trigonal Cu atom [Cu–Cl 2.216(3)–2.238(2) Å] are shorter than the Cu–Cl distances of the square-pyramidal Cu atoms [Cu–Cl 2.370(2)–2.607(2) Å] and octahedral Cu atom [Cu–Cl 2.696(2)–2.839(2) Å]. The Cu–Cl distances of the trigonal copper atoms are in the typical range of the Cu^{I}–Cl distances, and those of the square-pyramidal and octahedral copper atoms are in the normal range of the Cu^{II}–Cl distances.[10] The Cu^{I}–Cu^{I}, Cu^{II}–Cu^{II}, and Cu^{I}–Cu^{II} distances are 3.521(2)–3.777(2), 3.850(1)–4.625(1), and 3.375(1)–5.420(2) Å, respectively.

The optical absorption spectrum of **1** in dmf contains features at $\lambda_{max} = 266$ nm (ε 14200 M^{-1} cm^{-1}), 378 nm (5700), and 620 nm (940). The intense former two absorptions in the UV region can be attributed to chloro-to-Cu^{II} and thiolato-to-Cu^{II} charge transfer transitions, respectively.[11,12] The absorption in the visible region can be assigned to ligand field transitions of the $Cu^{II}N_2SCl_2$ and $Cu^{II}N_2SCl_3$ moieties. Since the IT band was not observed in this complex, the charge of the metal ions seems to be fully localized.

The magnetic moment of **1** at room temperature (2.1 BM) suggests that a strong antiferromagnetic interaction is operating between the Cu^{II} ions. The magnetic moments of **1** measured to 4.5 K are plotted in Figure 2. The magnetic data were analyzed with van Vleck equation including a Weiss temperature θ based on the Heisenberg model [$H = -2J\boldsymbol{S}_{Cu2} \cdot \boldsymbol{S}_{Cu3} - 2J'(\boldsymbol{S}_{Cu2} \cdot \boldsymbol{S}_{Cu5} + \boldsymbol{S}_{Cu3} \cdot \boldsymbol{S}_{Cu5})$].[13] The best fitting parameters are $J = -602\,cm^{-1}$, $J' = -2.5\,cm^{-1}$, $g = 2.06$, $\theta = -0.91$ K. The result shows that a strong antiferromagnetic interaction mainly occurs between the Cu2 and Cu3 atoms. The bond distances of Cu2-Cl3 [2.370(2) Å] and Cu3–Cl3 [2.396(2) Å] are significantly shorter than those of Cu2–Cl2, Cu5–Cl2, Cu5–Cl5, and Cu3–Cl5 [2.557(2)–2.839(2) Å] and the Cu2–Cl3–Cu3 angle is 152.07(9) °. This feature may contribute to the strong antiferromagnetism of **1**, because a larger antiferromagnetic coupling would be expected as the bridging angle increases.

At present, this kind of $Cu^{I}Cu^{II}$ mixed-valence complex has not yet be isolated by the use of unmethylated ligand, Hapaet. Hence, methyl groups of the present ligand may be favorable to the formation of the mixed-valence state, because the substituent groups adjacent to the thiolato-sulfur may protect the Cu^{I} ions against oxidation by the steric hindrance. Further study is now underway in our laboratory.

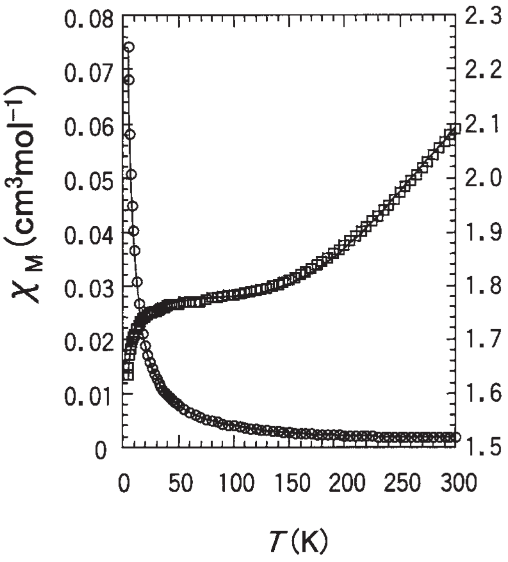


Figure 2. Magnetic susceptibility data (○) and effective magnetic moments (□) of **1**. The solid lines were calculated from the van Vleck equation based on the Heisenberg model.[13]

References and Notes

1 For example, see B. Krebs and G. Henkel, *Angew. Chem., Int. Ed. Engl.*, **30**, 769 (1991).

2 R. P. Houser, V. G. Young, Jr., and W. B. Tolman, *J. Am. Chem. Soc.*, **118**, 2101 (1996); R. P. Houser and W. B. Tolman, *Inorg. Chem.*, **34**, 1632 (1995).

3 M. Handa, M. Mikuriya, J.-Z. Zhuang, H. Okawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **61**, 3883 (1988).

4 M. Mikuriya, T. Kotera, F. Adachi, M. Handa, M. Koikawa, and H. Okawa, *Bull. Chem. Soc. Jpn.*, **68**, 574 (1995); M. Mikuriya, H. Tsutsumi, R. Nukada, M. Handa, and Y. Sayama, *Bull. Chem. Soc. Jpn.*, **69**, 3489 (1996); M. Mikuriya, X. Jian, S. Ikemi, T. Kawahashi, and H. Tsutsumi, *Bull. Chem. Soc. Jpn.*, **71**, 2161 (1998).

5 M. Mikuriya, F. Adachi, H. Iwasawa, M. Handa, M. Koikawa, and H. Okawa, *Bull. Chem. Soc. Jpn.*, **67**, 3263 (1994); M. Mikuriya, X. Jian, S. Ikemi, T. Kawahashi, H. Tsutsumi, A. Nakasone, and J.-W. Lim, *Inorg. Chim. Acta*, **312**, 183 (2001).

6 M. Mikuriya and T. Kotera, *Chem. Lett.*, **1998**, 971; T. Kawahashi, M. Mikuriya, R. Nukada, and J.-W. Lim, *Bull. Chem. Soc. Jpn.*, **74**, 323 (2001).

7 A toluene solution of isobutylene sulfide (8.6 g/50 cm^3) was added dropwise to a toluene solution (200 cm^3) containing 1,3-diaminopropane (74.1 g). The mixture was heated at reflux for 2 h. The product was collected by distillation at 79–81 °C/5 mmHg and 10.4 grams of Hapampt was obtained.

8 All maniplations were performed under argon by using standard Schlenk techniques.

9 Crystallographic data: for $\mathbf{1}\cdot 2CH_3OH$; $C_{23}H_{59}Cl_6Cu_6N_6O_2S_3$ fw = 1141.88, orthorhombic, space group *Pbca*, $a = 18.706(5)$, $b = 18.283(5)$, $c = 23.962(6)$ Å, $V = 8195(4)$ $Å^3$, $Z = 8$, $d_{calcd} = 1.85$ gcm^{-3}, μ(Mo Kα) = 36.34 cm^{-1}, 33826 reflections collected, 5936 independent reflections, $R1[I > 2\sigma(I)] = 0.048$, $wR2\,[I > 2\sigma(I)] = 0.110$. Intensity data were collected on a Bruker CCD X-ray diffractometer using graphite-monochromated Mo-Kα radiation. The structure was solved by the direct method and refined by the full-matrix least-squares method using a SHELXTL software package.

10 M. Dunaj-Jurco, G. Ondrejovic, and M. Melnik, *Coord. Chem. Rev.*, **83**, 1 (1988).

11 P. K. Bharadwaj, E. John, C.-L. Xie, D. Zhang, D. N. Hendrickson, J. A. Potenza, and H. J. Schugar, *Inorg. Chem.*, **25**, 4541 (1986).

12 V. M. Miskowski, J. A. Thich, R. Solomon, and H. J. Schugar, *J. Am. Chem. Soc.*, **98**, 8344 (1976).

13 B. N. Figgis and J. Martin, *J. Chem. Soc, Dalton Trans.*, **1972**, 2174.