Inorg. Chem. **2006**, *45*, 3452–3455

Inorganic Chemistry
Article

Synthesis and Characterization of Rhenium–Copper Sulfide Cluster Complexes $[(Ph_3P)_2N][Re_3(CuX)(\mu_3\text{-}S)_4Cl_6(PMe_2Ph)_3]$ (X = Cl, Br, I)

Kazuya Iijima, Tomoaki Sunaga, Masaya Hirose, and Taro Saito*

Department of Chemistry, Faculty of Science, Kanagawa University,
Hiratsuka, Kanagawa 259-1293, Japan

Received December 13, 2005

The reaction of a trinuclear rhenium sulfide cluster compound $Re_3S_7Cl_7$ with dimethylphenylphosphine and CuX_2 (X = Cl or Br) or CuX (X = Cl, Br, or I) formed tetranuclear cluster complexes $[(Ph_3P)_2N][Re_3(CuX)(\mu_3\text{-}S)_4Cl_6(PMe_2Ph)_3]$ (X = Cl, Br, or I). Their solutions have the characteristic intense blue color with visible spectral bands near 600 nm. Single-crystal X-ray structures show that three μ-S atoms in the intermediate trinuclear rhenium complex coordinate to a copper atom, forming elongated tetrahedral structures in which Re–Cu bonding interaction is negligible (Re–Cu distances are 3.50∼3.54 Å as compared with Re–Re distances ranging from 2.69 to 2.81 Å).

Introduction

Fragment condensation is one of the three general methods of cluster synthesis and, apparently, is more useful than the self-assembly of mononuclear species and excision from solid-state cluster compounds because of the versatility and higher predictability of the cluster frameworks.[1,2] Since Shibahara et al. reported the condensation of $[Mo_3S_4]^{4+}$ with Fe in 1986,[3] a number of cubane cluster compounds of molybdenum and tungsten with heterometals $[M_3M'Y_4]^{n+}$ (M = Mo or W; Y = S or Se; M′ = Cr, Mo, W, Fe, Co, Ni, Pd, Cu, Hg, Ga, In, Tl, Sn, Pb, Sb, or Bi) have been synthesized.[4−9] Despite our hope to prepare isoelectronic Re(V) analogues,[10] only $[Re_3NiS_4Cl_6(PEt_3)_4]^-$[11] and $[Re_3CoS_4Cl_6(PMe_2Ph)_4]$[12] have been reported. This is due partly to the situation that only one starting compound, $Re_3S_7Cl_7$,[13] is available as a building unit, which is not always easy to prepare, and to the difficulty of performing condensation reactions of the Re_3S_4 unit with heterometals. Several $[M_3CuY_4]^{n+}$ (M = Mo or W; Y = S or Se) complexes are known,[14−25] but $[Re_3CuS_4]$ cluster compounds have not been reported. There are some known examples of rhenium−copper mixed-metal sulfide cluster compounds with different

---

* To whom correspondence should be addressed. E-mail: saito-tr@chem.kanagawa-u.ac.jp.

(1) Saito, T. Chalcogenide Cluster Complexes of the Early Transition Metals. In *Early Transition Metal Clusters with π-Donor Ligands*; Chisholm, M. H., Ed.; VCH: New York, 1995; pp 63−164.
(2) Gray, T. G. *Coord. Chem. Rev.* **2003**, *243*, 213.
(3) Shibahara, T.; Akashi, H.; Kuroya, H. *J. Am. Chem. Soc.* **1986**, *108*, 1342.
(4) Shibahara, T. *Adv. Inorg. Chem.* **1991**, *37*, 143.
(5) Sokolov, M. N.; Fedin, V. P.; Sykes, A. G. Chalcogenide-Containing Metal Clusters. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: New York, 2004; pp 761−823.
(6) Hernandez-Molina, R.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1999**, 3137.
(7) Saysell, D. M.; Sokolov, M. N.; Sykes, A. G. In *Transition Metal Sulfur Chemistry*; Stiefel, E. I., Matsumoto, K., Eds.; American Chemical Society: Washington, D. C., 1996; ACS Symposium Series, *653*, pp 216−224.
(8) Sakane, G.; Shibahara, T. In *Transition Metal Sulfur Chemistry*; Stiefel, E. I., Matsumoto, K., Eds.; American Chemical Society: Washington, DC, 1996; ACS Symposium Series, *653*, pp 225−239.
(9) Sakane, G.; Shibahara, T. *Inorg. Synth.* **2002**, *33*, 150.
(10) Saito, T. *J. Chem. Soc., Dalton Trans.* **1999**, 97.
(11) Miyake, N.; Imoto, H.; Saito, T. *Chem. Lett.* **1997**, 631.
(12) Sakai, N.; Saito, T. *Polyhedron* **2004**, *23*, 2611.
(13) Timoshchenko, N. N.; Kolosnichenko, V. L.; Volkov, S. V.; Slovokhotov, Y. L.; Struchkov, Y. T. *Koord. Khim.* **1990**, *16*, 1062.
(14) Wu, X.; Lu, S.; Zu, L.; Lu, J. *Inorg. Chim. Acta* **1987**, *133*, 39.
(15) Zhan, H.; Zheng, Y.; Wu, X.; Lu, J. *Inorg. Chim. Acta* **1989**, *156*, 277.
(16) Lu, S.; Zhu, N.; Wu, X.; Wu, Q.; Lu, J. *J. Mol. Struct.* **1989**, *197*, 15.
(17) Zheng, Y.; Zhan, H.; Wu, X. *Acta Crystallogr., Sect C* **1989**, *45*, 1990.
(18) Lu, S. F.; Huang, J. Q.; Chen, Z. D.; Wu, Q. J.; Chen, W. Z.; Huang, X. Y.; Huang, Z. X.; Huang, J. L.; Lu, J. X. *J. Cluster Sci.* **1992**, *3*, 179.
(19) Diller, H.; Keck, H.; Kuchen, W.; Mootz, D.; Wiskemann, R. *Z. Naturforsch., B: Chem. Sci.* **1993**, *48*, 291.
(20) Diller, H.; Keck, H.; Wunderlich, H.; Kuchen, W. *J. Organomet. Chem.* **1995**, *489*, 123.
(21) Hegetschweiler, K.; Worle, M.; Meienberger, M. D.; Nesper, R.; Schmalle, H. W.; Hancock, R. D. *Inorg. Chim. Acta* **1996**, *250*, 35.
(22) Akashi, H.; Shibahara, T. *Inorg. Chim. Acta* **1998**, *282*, 50.
(23) Akashi, H.; Shibahara, T. *Inorg. Chim. Acta* **2000**, *300−302*, 572.
(24) Llusar, R.; Uriel, S.; Vicent, C. *J. Chem. Soc., Dalton Trans.* **2001**, 2813.
(25) Feliz, M.; Garriga, J. M.; Llusar, R.; Uriel, S.; Humphrey, M. G.; Lucas, N. T.; Samoc, M.; Luther-Davies, B. *Inorg. Chem.* **2001**, *40*, 6132.

10.1021/ic052135h CCC: \$33.50

Table 1. Crystallographic Data for **1**, **2**, and **3**

	1	**2**	**3**
empirical formula[a]	$C_{62}H_{67}Cl_{11}CuNP_5Re_3S_4$	$C_{62}H_{67}BrCl_{10}CuNP_5Re_3S_4$	$C_{61}H_{65}Cl_8CuINP_5Re_3S_4$
fw	2121.35	2165.81	2127.87
cryst size (mm^3)	0.35 × 0.20 × 0.10	0.14 × 0.04 × 0.02	0.36 × 0.10 × 0.03
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a (Å)	11.1274(5)	11.1389(5)	11.1246(8)
b (Å)	14.6445(6)	14.6844(6)	14.0736(10)
c (Å)	45.975(2)	46.149(2)	46.934(4)
β (deg)	96.865(1)	96.792(1)	95.651(2)
V (Å^3)	7438.2(6)	7495.5(6)	7312.4(9)
Z	4	4	4
T (K)	173	173	90
radiation (Mo Kα)	0.710 69	0.710 69	0.710 69
ρ_{calc} (g cm^{-3})	1.894	1.919	1.933
μ (mm^{-1})	5.802	6.255	6.213
θ range (deg)	0.89−28.31	0.89−24.71	0.87−28.29
hkl index ranges	−13/14	−13/12	−13/14
	−19/18	−14/17	−18/18
	−55/61	−41/54	−60/62
reflns. collected	55 368	42 185	53 789
independent reflns.	18 477	12 736	18 133
abs correction	emprical	emprical	empirical
GOF on F^2	1.017	1.064	1.150
R1[b]/wR2[c] [$I > 2\sigma(I)$]	R1 = 0.0614	R1 = 0.0355	R1 = 0.0852
	wR1 = 0.1952	wR2 = 0.1268	wR2 = 0.1297
R (all data)	R1 = 0.1048	R1 = 0.0759	R1 = 0.1032
	wR2 = 0.1458	wR2 = 0.1427	wR2 = 0.2062
largest diff peak and hole	3.725, −2.201	3.574, −2.075	6.841, −2.981

[a] Including solvate molecules. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma F_o$ [c] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$

metal frameworks.[26−28] During the course of our studies on mixed-metal rhenium cluster complexes, we found that copper halides gave Re_3Cu cluster complexes with unexpectedly distorted structures. This paper describes the syntheses and structures of these cluster complexes.

Experimental Section

Materials and Methods. Most of the experiments were carried out under dinitrogen using standard Shlenk techniques unless otherwise stated. Rhenium metal, dimethylphenylphosphine, and bis(triphenylphosphoranylidene)ammonium chloride ($[(Ph_3Ph)_2N]Cl$) were purchased from Aldrich, and $CuCl_2$, $CuBr_2$, and CuI were purchased from WAKO chemicals, and they were used as received. $Re_3S_7Cl_7$ was prepared according to the literature.[13] Solvents were dried and distilled by the standard methods. Electronic spectra were recorded on a JASCO Ubest-570 UV−vis spectrometer. ^1H and ^{31}P NMR spectra were measured in $CDCl_3$ with a JEOL GX-400 spectrometer. X-ray photoelectron spectrometry (XPS) spectra were measured on a JEOL JPS-9010 spectrometer. Electron spin resonance (ESR) spectra of solid samples or 2.5×10^{-4} M solutions in CH_2Cl_2 of **1** were recorded on a JEOL JES-RE2X X-band spectrometer.

$[(Ph_3P)_2N][Re_3(CuCl)S_4Cl_6(PMe_2Ph)_3].2CH_2Cl_2$ (1). *Method 1.* $Re_3S_7Cl_7$ (0.52 g, 0.51 mmol) was treated with PMe_2Ph (0.5 mL) in CH_2Cl_2 (20 mL) for 2 days at room temperature. $CuCl_2$ (0.07 g, 0.52 mmol) in EtOH (5 mL) and a few drops of PMe_2Ph were added to the solution. After stirring for 3 days, the mixture was filtered, and volatile materials were removed under reduced pressure. The residue was washed with Et_2O (3 × 5 mL). The product was dissolved in CH_2Cl_2 (10 mL), and $[(Ph_3P)_2N]Cl$ (0.29 g, 0.51 mmol) was added to the solution, which was stirred for 2 h. Et_2O (15 mL) was layered on the solution, which was left for 2 days. Black crystals (0.50 g, 47% yield) were obtained after filtration, washing with Et_2O, and drying. Anal. Calcd for $C_{62}H_{67}Cl_{11}CuNP_5Re_3S_4$: C, 35.10; H, 3.18; N, 0.66. Found: C, 35.36; H, 3.15; N, 0.67. UV−vis (CH_2Cl_2) λ_{max}, nm (ϵ): 601 (3312), 690 (sh), 880 (∼500). ^1H NMR (400 MHz, $CDCl_3$): δ 2.17 (d, Re−P*Me*$_2$Ph), 7.32∼7.76 [m, PMe_2*Ph*, (*Ph*$_3$P)$_2$N$^+$]. ^{31}P NMR (161.7 MHz, $CDCl_3$, 15% H_3PO_4): δ −39.47 (*P*Me$_2$Ph), 22.49 [(Ph$_3$*P*)$_2$N$^+$].

Method 2. A similar experimental procedure was followed except using an ethanol solution of CuCl without the addition of extra phosphine.

$[(Ph_3P)_2N][Re_3(CuBr)S_4Cl_6(PMe_2Ph)_3]\cdot 2CH_2Cl_2$ (2). *Method 1.* A similar procedure to that used for **1**, but using $CuBr_2$, was followed. Yield: 0.57 g, 52%. Anal. Calcd for $C_{62}H_{67}BrCl_{10}CuNP_5Re_3S_4$: C, 34.38; H, 3.12; N, 0.65. Found: C, 34.58; H, 3.11; N, 0.68. UV−vis (CH_2Cl_2) λ_{max}, nm (ϵ): 604 (4561), 880 (∼500). ^1H NMR (400 MHz, $CDCl_3$): δ 2.17 (d, Re−P*Me*$_2$Ph), 7.32∼7.76 [m, PMe_2*Ph*, (*Ph*$_3$P)$_2$N$^+$]. ^{31}P NMR (161.7 MHz, $CDCl_3$, 15% H_3PO_4): δ −39.55 (*P*Me$_2$Ph), 21.50 [(Ph$_3$*P*)$_2$N$^+$].

Method 2. A similar experimental procedure was followed except using an ethanol solution of CuBr without the addition of extra phosphine.

$[(Ph_3P)_2N][Re_3 (CuI)S_4Cl_6(PMe_2Ph)_3]\cdot CH_2Cl_2$ (3). A procedure similar to that for **1** was followed, but using CuI without the addition of extra PMe_2Ph. Yield: 0.57 g, 55%. Anal. Calcd for $C_{61}H_{65}Cl_8CuINP_5Re_3S_4$: C, 34.43; H, 3.08; N, 0.66. Found: C, 34.51; H, 3.22; N, 0.63. UV−vis (CH_2Cl_2) λ_{max}, nm (ϵ): 610 (5522). ^1H NMR (400 MHz, $CDCl_3$): δ 2.18 (d, Re−P*Me*$_2$Ph), 7.28∼7.76 [m, PMe_2*Ph*, (*Ph*$_3$P)$_2$N$^+$]. ^{31}P NMR (161.7 MHz, $CDCl_3$, 15% H_3PO_4): δ −39.55 (*P*Me$_2$Ph), 21.50 [(Ph$_3$*P*)$_2$N$^+$].

X-ray Crystal Structure Determination. Crystals suitable for X-ray crystallography were prepared by recrystallization of the products from CH_2Cl_2 and Et_2O over a few days. Data were collected on a Bruker Smart APEX CCD system with a graphite monochromated Mo Kα radiation source. Crystals were transferred

---

(26) Scattergood, C. D.; Garner, C. D. *Inorg. Chim. Acta* **1987**, *132*, 161.
(27) Simonnet-Jegat, C.; Halut, S.; Secheresse, F. *J. Cluster Sci.* **1996**, *7*, 677.
(28) Müller, A.; Krickemeyer, E.; Bögge, H.; Penk, M. *Chimia* **1989**, *43*, 319.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for Compounds **1**, **2**, and **3**

	1	**2**	**3**
	Distances		
Re(1)−Re(2)	2.7088(5)	2.7110(6)	2.7010(8)
Re(1)−Re(3)	2.7045(6)	2.7039(7)	2.7147(7)
Re(2)−Re(3)	2.6959(5)	2.6989(6)	2.6904(7)
Re(1)−Cu(1)	3.548	3.539	3.522
Re(2)−Cu(1)	3.511	3.506	3.535
Re(3)−Cu(1)	3.543	3.541	3.506
Re−S (av)	2.312	2.310	2.313
Cu(1)−Cl(7)	2.145(3)		
Cu(1)−Br(1)		2.236(2)	
Cu(1)−I(1)			2.412(2)
Cu(1)−S (av)	2.389	2.386	2.378
Re−P (av)	2.534	2.536	2.531
Re−Cl (av)	2.414	2.423	2.421
N(1)−P(av)	1.586	1.581	1.580
	Angles		
Re(3)−Re(1)−Re(2)	59.736(14)	59.790(16)	59.574(18)
Cl(7)−Cu(1)−S(1)	121.22(11)		
Cl(7)−Cu(1)−S(2)	138.88(11)		
Br(1)−Cu(1)−S(1)		119.57(11)	
Br(1)−Cu(1)−S(2)		138.72(10)	
I(1)−Cu(1)−S(1)			129.79(11)
I(1)−Cu(1)−S(3)			124.83(12)
S(1)−Cu(1)−S(2)	81.01(9)	80.99(11)	79.80(10)
Cu(1)−S(1)−Re(1)	97.86(9)	97.73(10)	96.82(10)
Cu(1)−S(2)−Re(2)	97.80(9)	97.62(10)	98.67(11)
Cu(1)−S(3)−Re(1)	97.70(8)	97.61(10)	97.79(11)
Re(2)−S(1)−Re(1)	72.17(2)	73.25(4)	72.34(9)
Re(1)−S(4)−Re(2)	71.01(6)	73.24(4)	70.53(9)
P(1)−Re(1)−Re(3)	136.79(6)	146.48(4)	138.32(8)
P(1)−Re(1)−Re(2)	137.66(6)	101.79(4)	134.61(8)
Cl(1)−Re(1)−Cl(2)	85.78(9)	84.83(8)	85.43(13)
P(1)−Re(1)−Cl(1)	78.37(9)	78.53(6)	79.45(13)
P(1)−Re(1)−Cl(2)	79.98(9)	80.20(5)	79.66(14)

to the goniostat where **1** and **2** were cooled to −100 °C and **3** to −183 °C for data collection. The data were collected using 15 s frames with an Ω scan of 0.30° and were corrected for Lorentz and polarization effects. Absorption corrections were applied using the SADABS empirical method. Data were treated by the Bruker SAINT software, and the structures were solved using SHELXTL.[29] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added at calculated positions and included in the final refinement. Eight solvent (CH_2Cl_2) molecules were found in a unit cell of **1** and **2** and four in a unit cell of **3**. Crystallographic data are given in Table 1.

Results and Discussion

Synthesis and Characterization. Reactions of $Re_3S_7Cl_7$ with dimethylphenylphosphine followed by the addition of copper(II) chloride or bromide in the presence of dimethylphenylphosphine or by the addition of copper(I) iodide formed the rhenium−copper mixed-metal cluster complexes $[(Ph_3P)_2N][Re_3(CuX)S_4Cl_6(PMe_2Ph)_3]$ (X = Cl, **1**; Br, **2**; or I, **3**). Originally, the Re_3Cu cluster complexes **1** and **2** were obtained using copper(II) chloride or bromide as a copper source, and we found, subsequently, that the addition of a small amount of dimethylphenylphosphine to the reaction solution improved the yield. We assumed that extra phosphine reduced Cu(II) to Cu(I) and made the formation of the cluster complexes smoother. Structural analyses and NMR measurements suggested that copper is in the Cu(I) state in the cluster complexes, and the assignment of the copper as Cu(I) has been supported by the silence of ESR signals of Cu(II) and by XPS. We found that copper(I) halides could also be used for the syntheses with comparable yields.

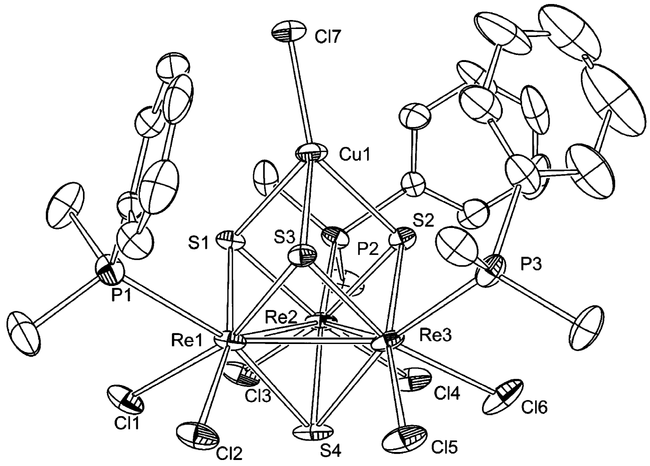

Figure 1. ORTEP (50%) structure of $[Re_3CuCl(\mu_3\text{-}S)_4Cl_6(PMe_2Ph)_3]^{1-}$. Hydrogen atoms are omitted for clarity.

Dichloromethane solutions of the products are blue with a strong characteristic band near 600 nm in the visible spectra. Among a few heterometals so far tried,[12] copper is the best in giving good yields of the tractable products. This may be related to a better affinity of copper to sulfur or a tendency of the metal to form tetra metal clusters without Re−Cu bonds (vide infra).

Structures. The interatomic distances and angles for **1**−**3** are given in Table 2. The cluster anion structure of 1 is illustrated in Figure 1. The cluster frameworks of compounds **1**−**3** are elongated tetrahedra with Re−Re distances of 2.69−2.71 Å and Re−Cu distances of 3.50−3.54 Å. The S−Cu−S angles range from 79.8 to 81.0°, reflecting relatively long Re−Cu distances. Long Re−Cu distances indicate a lack of bonding interaction between rhenium and copper atoms. This is unique to the present $[Re_3CuS_4X_7(PMe_2Ph)_3]^{1-}$ (62 e$^-$) clusters because $[Re_3CoS_4Cl_6(PMe_2Ph)_4]$ (60 e$^-$)[12] and $[Re_3NiS_4Cl_6(PEt_3)_4]$ (61 e$^-$)[11] as well as $[M_3CuS_4(H_2O)_{10}]^{5+}$ (M = Mo or W) (60 e$^-$) cluster complexes have much shorter Re−M (Re−Co, 2.60∼2.61 Å; Re−Ni, 2.67∼2.77 Å), Mo−Cu (2.80∼2.92 Å),[14,16,18−25,30,31] or W−Cu (2.82∼2.96 Å)[15,17] distances, which invoke metal−metal bonds. In the case of cobalt, two cluster isomers with different orientations of PMe_2Ph were obtained, depending on the reaction temperatures.[12] The main product of the Re_3Co cluster has three dimethylphenylphosphine orientations opposite Co, whereas the orientation of dimethylphenylphosphine ligands in **1**−**3** is directed to Cu. In the case of the Re_3Co cluster, phosphine flipping from the orientation in the starting Re_3 cluster was required and a higher temperature of the synthetic reaction was favorable for the change. We first thought that interaction of the μ-S ligands with Cu was so strong that the trinuclear

---

(29) *SHELXTL-NT*, version 6.12; Bruker Axis, Inc.: Madison, WI, 2001.

(30) Nasreldin, M.; Li, Y. J.; Mabbs, F. E.; Sykes, A. G. *Inorg. Chem.* **1994**, *33*, 4283.

(31) Lu, S.; Chen, H. B.; Huang, J. Q.; Wu, Q. J.; Sun, Q. L.; Li, J.; Lu, J. X. *Inorg. Chim. Acta* **1995**, *232*, 43.

cluster $[Re_3S_4Cl_6(PMe_2Ph)_3]^{1-}$ [32] captured a Cu atom before the flipping isomerization of phosphine ligands occurred. Three phosphine ligands probably prevent the approach of a copper atom to the Re_3 plane, resulting in the longer Re−Cu distances. We then attempted to prepare putative isomers of the Re_3Cu clusters with Re−Cu bonds and an opposite orientation of dimethylphosphine ligands by raising the reaction temperature in refluxing toluene but obtained only the same product. It is likely that the number of cluster valence electrons (62 e^-) is too high to form Re_3Cu cluster complexes with Re−Cu bonds, but we are still seeking a better explanation to account for the remarkable difference.

Three Re_3Cu cluster complexes with different Cu−X (X = Cl, Br, and I) bonds show only small differences of Cu−X distances (2.14∼2.41 Å), reflecting the ionic radii of X, but there is no significant difference of the geometry of the Re_3 cluster frameworks. Because no Re−Cu bonds exist, X does not affect the electronic and geometrical states of the Re_3 cluster system. For example, absorption maxima in visible spectra are similar and chemical shifts of phosphine ligands in ^1H and ^{31}P NMR spectra are almost the same.

XPS Spectra. XPS spectra of cluster complex **1** were measured to determine the oxidation states of the copper and rhenium in the complex. The binding energies are 932.6 eV for $Cu_{2p3/2}$ and 41.9 and 44.4 eV for $Re_{4f7/2}$. Generally, the chemical shifts of copper compounds are small, and identical compounds sometimes give different values.[33] However, Cu(I) compounds usually give lower binding energies than Cu(II) compounds. It is more reasonable to assign the value of complex **1** to Cu(I) (d^{10}) than to Cu(II) (d^9). This conclusion is supported by the silence of ESR signals characteristic of Cu(II). Rhenium peaks are assigned to Re(IV) (41.9 eV) and Re(V) (44.4 eV). Thus, the cluster ion is expressed as $[Re(V)Re(IV)_2Cu(I)S_4Cl_6]^{1-}$. The copper ion in $[Mo_3CuS_4]^{5+}$ cubes has been assigned to Cu(I) from the XPS data ($Cu_{2p3/2}$, 933.4 eV).[23]

ESR Spectra. ESR spectra of compound **1** both in the solid states and in solutions in CH_2Cl_2 at room temperature showed only very weak bands probably due to minor impurities. Therefore, we judged that the copper ion in the cluster is not Cu(II).

Visible Spectra. The Re_3Cu cluster complexes **1**, **2**, and **3** show strong bands at 601−610 nm with a shoulder and a weak band near 900 nm. Copper(I) compounds have d^{10} electron configurations and are usually colorless, except for those with color resulting from the anion or charge-transfer bands.[34] Cluster complexes **1**−**3** show a deep blue color, and the main spectral bands near 600 nm (ϵ 3312∼5522) look very much like those of blue copper proteins. The strong bands in blue copper proteins are assigned to the charge transfer (CT) from S to Cu(II) in the distorted tetrahedral environments.[35−38] Judging from the synthetic procedures using Cu(I) halides, chemical compositions, ESR spectra, and the XPS of the cluster complex **1**, it is reasonable to regard the copper in the clusters as Cu(I). If the copper is in a d^{10} state, no d−d bands are expected. Therefore, the bands in the cluster complexes **1**−**3** must be due to CT bands. The preliminary molecular orbital calculations on **1** performed by the Gaussian03 program indicate that the main band at 601 nm is due to the transition from a degenerate electron orbital composed mainly of Cu + Cl to a degenerate electron orbital composed mainly of Re + S + Cl.[39] The blue color with high extinction coefficients (3312 M^{-1} cm^{-1}) matches that of blue copper proteins, but the origin of the color is unlikely of a ligand-to-metal CT from S to Cu.[35−38]

The Re_3Cu cluster complexes described here are unique in having no Re−Cu bonds. The clusters are composed formally of a Cu(I) and $Re(V)Re(IV)_2$ moieties. These complexes provide a new series of Cu(I) complexes coordinated by a Re_3 cluster as a tridentate sulfur ligand.

Acknowledgment. We thank Dr. Toshihiro Miyao of Kanagawa University for the measurements of the XPS spectra.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. X-ray crystallographic data reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-290942 (**1**), CCDC-290943 (**2**), and CCDC-290944 (**3**). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

IC052135H

---

(32) Saito, T.; Sunaga, T.; Sakai, N.; Nakamura, Y.; Yamamoto, S.; Iriuchijima, D.; Yoza, K. *Inorg. Chem.* **2005**, *44*, 4427.

(33) Database, N. X. http://srdata.nist.gov/xps/Cs_both_cs_dat.asp (accessed Nov 2005).

(34) Cotton, F. A.; Wikinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999; p 858.

(35) Sykes, A. G. *Adv. Inorg. Chem.* **1991**, *36*, 377.

(36) Solomon, E. I.; Szilagyi, R. K.; George, S. D.; Basumallick, L. *Chem. Rev.* **2004**, *104*, 419.

(37) Solomon, E. I.; Penfield, K. W.; Wilcox, D. E. *Struct. Bonding* **1983**, *53*, 1.

(38) Randall, D. W.; George, S. D.; Hdeman, B.; Hodgson, K. O.; Fujisawa, K.; Solomon, E. I. *J. Am. Chem. Soc.* **2000**, *122*, 11620.

(39) Tsuge, K.; Saito, T. To be published.