Inorganic Chemistry

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Copper Ion Mediated Selective Cleavage of C−S Bond in Ferrocenylthiosemicarbazone Forming Mixed Geometrical $[(PPh_3)Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$ Having Cu_2S_2 Core: Toward a New Avenue in Copper−Sulfur Chemistry

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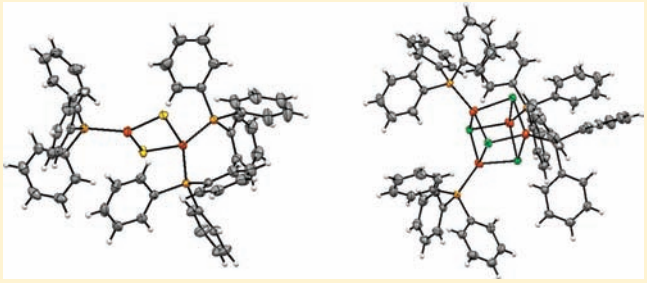
Supporting Information

ABSTRACT: Unprecedented selective cleavage of the carbon−sulfur bond of the ferrocenylthiosemicarbazone moiety has been observed for the first time, resulting in the formation of mixed geometrical binuclear copper complex $[(PPh_3)Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$. Upon trying direct synthesis of the title complex, an unusual tetranuclear $[Cu_4(\mu_3\text{-}Cl)_4(PPh_3)_4]$ cubane resulted.



INTRODUCTION

Transition metal and main group metal complexes of thiosemicarbazones have invited considerable interest for a variety of reasons, such as variable bonding properties, structural diversity, and pharmacological properties.[1] Copper chalcogenide compounds including clusters are of continuing interest in structural, synthetic, and materials chemistry,[2] while examples of copper/inorganic-sulfur active-site entities in biology were recently discovered in the case of two metalloenzymes (cytochrome C oxidase and nitrous oxide reductase).[3] Nitrous oxide reductase (N_2OR) has an active-site $\{(histidine)_7Cu_4S\}$ cluster (called Cu_Z), where nitrous oxide binds and is reduced in the terminal step in bacterial denitrification.[3] With these findings, there has been a surge of interest in relevant copper coordination chemistry, with goals including (1) the generation of discrete and tractable copper sulfide complexes, (2) the elucidation of their structure and spectroscopy, and (3) electrochemical study of the copper sulfide compound, that is, redox and/or atom-transfer reactivity patterns. Moreover, cleavage of the C−S bond is an important step in the removal of the sulfur from thiophene in the hydrodesulphurization (HDS) process.[4] Thiophene and its benzo derivatives represent abundant sulfur-containing impurities in coal and petroleum feedstocks and are among the most difficult to desulfurize.[5] Homogenous transition metal complexes are ideal for probing the mechanism of this process by allowing analysis of specific steps in the proposed HDS cycle.[6] In addition, such complexes can show reactivity patterns that differ from commercial HDS catalysts. Many obstacles will have to be overcome to make these systems usable in any real process, including supporting the homogeneous species on a heterogeneous support.

EXPERIMENTAL SECTION

Preparation of $[(PPh_3)Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$. To a hot solution of $[CuCl_2(PPh_3)_2]$ (66 mg; 0.1 mmol) in dichloromethane (20 cm^3) was added ferrocenylthiosemicarabzone [HFtsc] (92 mg; 0.2 mmol) in hot ethanol (20 cm^3). The mixture was refluxed for 6 h. The resulting reaction mixture was concentrated to about 10 cm^3, and the solvents were allowed for partial evaporation and kept at room temperature for further evaporation to yield two products. One is orange brown crystals, which could be separated mechanically under a microscope. Yield: 37% (36.04 mg). Mp 246 °C. FT-IR (KBr): 1430, 1085, 702 cm^{-1} (for PPh_3); 468 cm^{-1} $\nu_{(Cu-S)}$. UV−vis (methanol), λ_{max} [nm] (ε, M^{-1} cm^{-1}): 397(2465), 461(1655), 479(1406), 515(929), 554(539), 589(340), 631(140). Elemental analyses calcd. for $C_{54}H_{45}S_2P_2Cu_2$: C, 68.48; H, 4.79; S, 6.77%. Found: C, 68.42; H, 4.80; S, 6.72%. The compound dissolved in common organic solvents such as dichloromethane, chloroform, benzene, acetone, methanol, ethanol, DMF, and DMSO. Another product was a dark brown one, which did not dissolve in any organic solvent (yield: 48 mg). Hence, it was left without further characterization.

Preparation of $[Cu_4(\mu_3\text{-}Cl)_4(PPh_3)_4]$. $[CuCl_2(PPh_3)_2]$ (132 mg; 0.2 mmol) was refluxed in a 1:1 ethanol (20 cm^3)/dichloromethane (20 cm^3) mixture with elemental sulfur (6.5 mg; 0.2 mmol). A black

Received: October 22, 2011
Published: February 29, 2012

 © 2012 American Chemical Society dx.doi.org/10.1021/ic2022616 | Inorg. Chem. 2012, 51, 3525−3532

brown copper sulfide precipitated immediately, which was filtered, and the mother liquid was left for slow evaporation to yield white crystals. Yield: 9% (26.02 mg). M.p. > 250 °C. FT-IR (KBr): 1431, 1122, 693 cm^{-1} (for PPh_3). UV−vis (methanol), λ_{max} [nm] (ε, M^{-1} cm^{-1}): 269 (136 000), 274 (60 200), 310 (18 332). (^1H $CDCl_3$): δ 6.4−7.7 ppm (m, aromatic protons of PPh_3). Elemental analyses calcd. for $C_{72}H_{60}Cl_4P_4Cu_4$: C, 60.11; H, 4.18%. Found: C, 60.18; H, 4.23%. The compound dissolved in methanol, DMF, and DMSO. The same product was prepared by refluxing $[CuCl_2(PPh_3)_2]$ in a 1:1 ethanol/dichloromethane mixture for 5 h.

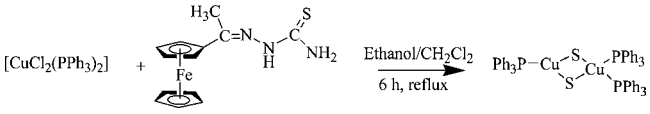
■ EXPERIMENTAL METHODS

C, H, N, and S analyses were performed using a Vario EL III elemental analyzer. IR spectra of the ligand and complexes have been recorded from KBr pellets with a Nicolet instrument in the 4000−400 cm^{-1} range. Electronic spectra of the complexes were measured in methanol using a Systronics 119 spectrophotometer in the 800−200 nm range. Melting points were recorded on a Loba India Melting point apparatus. The cyclic voltammetric studies were carried out in an acetonitrile window with a CH Instruments electrochemical analyzer using a platinum working electrode, and the redox potentials were referenced to a saturated Ag/AgCl electrode. Suitable single crystals for X-ray analysis were grown from a ethanol/dichloromethane mixture. The data were collected at 287 K with a Bruker Smart 1000 CCD Diffractometer using monochromated Mo Kα (λ = 0.71073 Å) radiation. The data were collected and processed using Saint, and the structures were solved and refined through full matrix least-squares on F^2 using SHELXTL 6.14. Electron paramagnetic resonance spectra (EPR) of the powder samples were recorded with a Jeol Tel-100 instrument at X-band frequencies at room and liquid nitrogen temperatures (77 K) using the 2,2-diphenyl-1-picrylhydrazyl radical (DPPH) as an internal standard. The ^1H NMR and ^{31}P NMR spectra were recorded with a Bruker AMX 400 instrument by using TMS and ortho-phosphoric acid as references, respectively.

■ RESULTS AND DISCUSSION

As a part of our systematic investigation on the reactions of thiosemicarbazones with various transition metal complexes,[7] a reaction between ferrocenylthiosemicarbazone (H-Ftsc)[8] and $[CuCl_2(PPh_3)_2]$[9] was carried out in order to obtain a hetero-trinuclear complex $[Cu(Ftsc)_2]$. But, a copper ion mediated selective cleavage of the carbon−sulfur bond of the ferrocenylthiosemicarbazone took place, leading to the formation of a mixed geometrical bis-μ_2-sulfido bridged bicopper complex (Scheme 1)

Scheme 1. Preparation of $[(PPh_3)Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$



along with the insoluble dark brown compound. This unprecedented selective cleavage of the C−S bond in the ferrocenylthiosemicabazone moiety deserves special attention due to its relevance to the HDS process.[6,10] Bis-μ_2-sulfido bridging in the complex essentially resulted *via* the selective cleavage of the carbon−sulfur bond of the ferrocenylthiosemicarbazone ligand. In this paramagnetic dicopper complex, the copper ions are in the +2 oxidation state with two different geometries. The formation of tri-coordinated copper complexes is also very rarely found in the literature.[11] A number of complexes might appear to be tri-coordinated, but upon close investigation they have been found to have higher coordination. The formation of tricoordinated complexes is favored mainly because of steric considerations over the normal four coordinated complexes. The formation of a sulfide (S^{2-}) moiety through the thermal decomposition through C−S bond cleavage of thiolate copper(II) complexes has been reported.[12] It is to be noted that the metal-sulfido clusters are important components in fundamental processes such as electron transfer and the reduction of dinitrogen.[13] In addition to this, to the best of our knowledge, the present work demonstrates the formation of the first example of a discrete mixed geometrical (trigonal planar and tetrahedral) dicopper complex having two bridging S^{2-} units between the copper ions. This is yet another interesting behavior exhibited by the thiosemicarbazone ligand. In this article, we report the synthesis, spectral characterization, crystal structure, DFT study, and electrochemistry of a bis-μ_2-sulfido dicopper complex.

The elemental analysis of the title complex $[(PPh_3)Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$ agreed very well with the proposed molecular formula. The calculated value of sulfur (6.77) is most reliable and relative to the found value (6.72) greatly supports the formation of the complex. The calculated values for carbon and hydrogen also matched very well with the found values. The observed differences between the calculated and found values are only 0.088%, 0%, and 0.739% for carbon, hydrogen, and sulfur, respectively. In the IR spectrum of the title complex, the absence of the bands at 823, 1651, and 3240 cm^{-1} corresponding to the $\nu_{C=S}$, $\nu_{C=N}$, and ν_{NH} indicates that the complex does not have a ferrocenylthiosemicarbazone moiety in it.[7b] However, a new band appeared at 468 cm^{-1} due to the presence of ν_{Cu-S}.[14] The UV−vis absorption spectrum of the title complex in methanol at room temperature contains a number of bands [λ_{max} [nm] (ε, M^{-1} cm^{-1})] at 397 (2465), 461 (1655), 479 (1406), 515 (929), 554 (539), 589 (340), and 631 (140). There is a noticeable difference in the charge transfer energy and intensity for these transitions. The intense absorptions in the visible region is an indication of the presence of sulfide bridge complexes. From the elemental analysis and IR spectrum of the insoluble polymeric compound, there was no appreciable information found. The EPR spectrum recorded at room temperature and liquid nitrogen temperature showed the EPR-silent nature of this compound (Figures S1 and S2, Supporting Information).

For X-ray single crystal studies, suitable crystals were obtained from ethanol/dichloromethane mixture by vapor diffusion method. The crystal structure of the complex is depicted in Figure 1. The extremely well ordered (R = 0.0394) unit cell contains a binuclear $[(PPh_3)Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$ in which Cu(1) is ligated in a tetrahedral P_2S_2 environment and Cu(2) is ligated in a trigonal planar PS_2 environment. The crystallographic parameters are given in Table 1. The observed shorter bond lengths of Cu(2)−S(1), 2.2448(6) Å; Cu(2)−S(2), 2.3091(7) Å; and Cu(2)−P(2), 2.1742(6) Å in the Cu(2)S(1)S(2)P(2) core compared to Cu(1)−S(1), 2.4049(7) Å; Cu(1)−S(2), 2.4503(7) Å; Cu(1)−P(1), 2.2357(7) Å; and Cu(1)−P(3), 2.2269(10) Å in the Cu(1)P(1)P(3)S(1)S(2) core may be due to less of a back bonding contribution of Cu(2) to P(2) phosphine than Cu(1) to P(1) and P(3) phosphines (Table 2). The variation in Cu−S bond lengths may be due to variation in the σ bonding contribution of the sulfide ion and the presence of back bonding triphenylphosphine groups in two different geometrical environments.[16] The Cu−P bond lengths have lengthened a little compared to other reported Cu−P values.[17] This lengthening may be due to the fact that the S^{2-} ligand is in coordination with two extensively back-bonded copper atoms. Such a kind of S^{2-} binegative

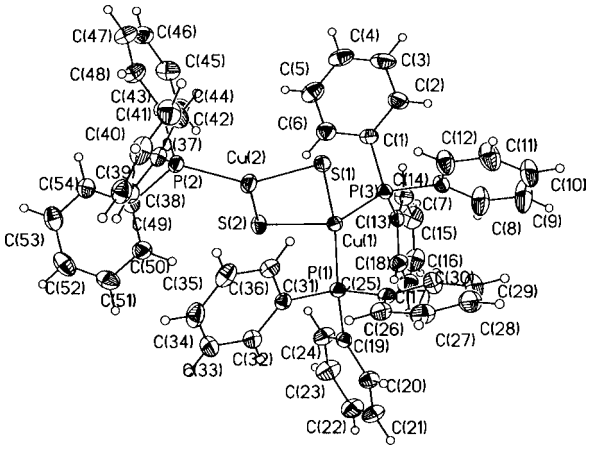


Figure 1. Structure of $[(PPh_3)Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$.

Table 1. Crystal Data and Structure Refinement for $[(PPh_3)Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$

empirical formula	$C_{54}H_{45}Cu_2P_3S_2$
fw	978.01
temp	173 K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	$P21/n$
unit cell dimensions	
a	18.999(4) Å
b	09.771(2) Å
c	26.359(5) Å
α	90°
β	109.56(3)°
γ	90°
volume	4610.88 Å^3
Z	4
calcd density	1.409 Mg/m^3
abs coeff	1.154 mm^{-1}
F(000)	2016
cryst size	1.1 × 0.7 × 0.3 mm
θ range for data collection	1.61−28.36°
limiting indices	$-25 \le h \le 24$, $-12 \le k \le 13$, $-34 \le l \le 35$
reflns collected/unique	54304/9136 [R(int) = 0.0387]
completeness to θ	28.36°
absorption correction	semiempirical from equivalents
refinement method	full-matrix least-squares on F^2
data/restraints/params	11268/0/550
Goodness-of-fit on F^2	0.755
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0394, wR2 = 0.0997
R indices (all data)	R1 = 0.0305, wR2 = 0.0951
largest diff. peak and hole	0.414 and −0.864 e.A^{-3}

behavior of sulfur has been observed elsewhere.[18] The Cu−Cu distance was found as 2.8988(5) Å, indicating the absence of direct metal metal bonding,[15] and the two Cu−S−Cu angles were found as 76.115(16)° and 75.863(15)°, respectively. S(1)−Cu(1)−S(2) and S(2)−Cu(2)−S(1) bond angles are 106.955(19)° and 97.835(17)°, respectively, indicating tetrahedral and trigonal planar geometry around the copper centers. Crystallographic data for $[(PPh_3)Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$ and $[Cu_4(\mu_3\text{-}Cl)_4(PPh_3)_4]$ have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication (CCDC No. 654122 and 847673). The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or

Table 2. Selected Structural Parameters (Bond Lengths in Å and Angles in Degrees) of $[(PPh_3)Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$ Obtained from X-Ray Crystallography and DFT Calculations

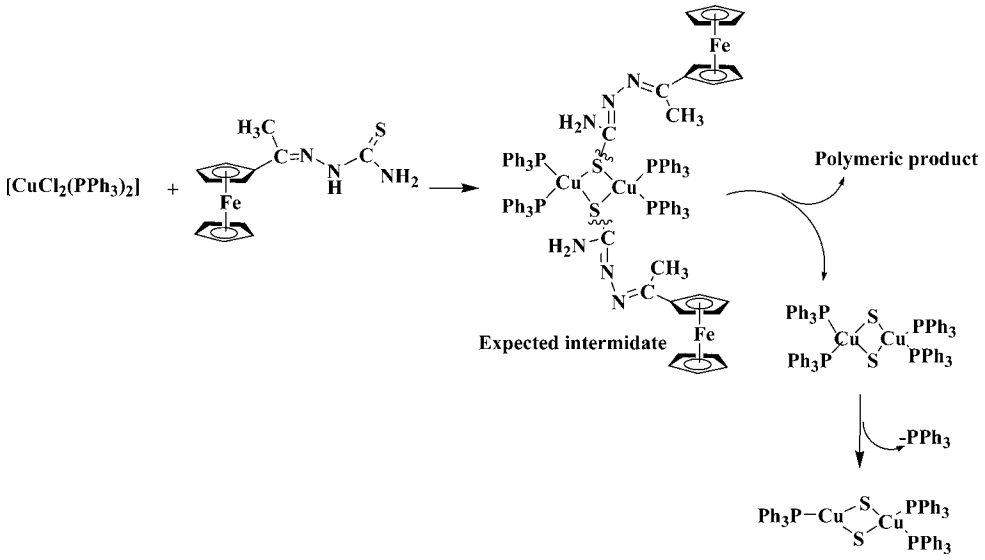
bond lengths	experimental	DFT
Cu1−Cu2	2.8988	2.6354
Cu1−S1	2.4503	2.4036
Cu1−S2	2.4049	2.4147
Cu1−P1	2.2357	2.4708
Cu1−P3	2.2269	2.3943
Cu2−S1	2.2448	2.2519
Cu2−S2	2.3091	2.2605
Cu2−P2	2.1742	2.332
bond angles [deg]	**experimental**	**DFT**
P3−Cu1−S1	102.328	100.7
P3−Cu1−S2	113.84	101.8
P3−Cu1−P1	131.38	123
P3−Cu1−Cu2	127.674	125.6
S1−Cu1−S2	97.835	101.4
S1−Cu1−P1	102.943	115.2
S1−Cu1−Cu2	48.743	52.8
S2−Cu1−P1	102.94	111.6
S2−Cu1−Cu2	50.574	52.9
P1−Cu1−Cu2	100.02	111.2
S1−Cu2−S2	106.955	111.5
S1−Cu2−P2	134.74	128.9
S1−Cu2−Cu1	55.142	58.2
S2−Cu2−P2	117.71	119.1
S2−Cu2−Cu1	53.563	58.5
P2−Cu2−Cu1	169.458	162.9
Cu2−S1−Cu1	76.115	68.8
Cu2−S2−Cu1	75.863	68.5
torsions angles [deg]		
atoms	**experimental**	**theoretical**
S2−Cu1−S1−Cu2	13.23(2)	22.283
P1−Cu1−S1−Cu2	−92.05(2)	−98.447
P3−Cu1−S1−Cu2	129.83(2)	126.899
S1−Cu1−S2−Cu2	−12.87(2)	−22.246
P1−Cu1−S2−Cu2	92.41(2)	100.977
P3−Cu1−S2−Cu2	−120.12(2)	−125.988
S2−Cu2−S1−Cu1	−14.29(2)	−25.262
P2−Cu2−S1−Cu1	175.19(2)	161.088
S1−Cu2−S2−Cu1	14.58(2)	25.199
P2−Cu2−S2−Cu1	−173.01(2)	−160.451

from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

The source of the sulfido ligand in $[(PPh_3)Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$ must be from the selective cleavage of the C−S bond of the thiosemicarbazone ligand, leading to the formation of a μ_2-sulfido bridged unsymmetrical bicopper complex. The expected mechanism for the formation of the unsymmetrical dicopper complex is given in Scheme 2. Recently, a few reports have appeared describing the binuclear copper complexes containing sulfur bridged thiosemicarbazones, and one among them is a tetranuclear cluster.[15] In our case, it is felt that such species may be an intermediate, and the carbon sulfur bond of the intermediate complex might have been cleaved during the course of the reaction.

The ground state geometry of the title compound has been optimized using a density functional theory (DFT) method employing Becke's three-parameter hybrid exchange functional

Scheme 2. Expected Mechanism of the Formation of $[(PPh_3)Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$



(B3)[19] combined with the correlation functional of Lee, Yang, and Parr (LYP),[20] together called B3LYP. The Los Alamos effective core potential (ECP) basis set, LanL2DZ[21−23] for the Cu atom and 6-311G(d.p) basis set for all other atoms have been used. The vibrational frequency calculation has been performed at the above level of theory, and the results confirm that the optimized geometry is at a stationary point of the potential energy surface without any imaginary frequency. The selective geometrical parameters obtained from single crystal X-ray data and DFT calculations are given in Table 2. The theoretical values are almost consistent with the experimental values. It has been observed that the root-mean-square deviation between single crystal X-ray data and optimized internal coordinates is 0.78 Å only. The density plot has been made with the isosurface value of 0.05 au. The DFT results from Mulliken atomic charges show that the Cu atom with two triphenylphosphines has more of a charge (−0.43 au) than the Cu with a single triphenylphosphine (−0.12 au). The frontier molecular orbital diagram shows that both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are mainly delocalized on the sulfur atoms and on the Cu atoms (Figures 2 and 3). There is a small amount of electron density corresponding to the LUMO being on the P3 atom of triphenylphosphine. The calculated energy gap between HOMO and LUMO is 3.54 eV (351 nm). This is comparable with the first intense absorption feature at 397. Hence, it is concluded that the absorption spectra observed at 397 nm are due to the transition of an electron from HOMO to LUMO. The DFT calculations were carried out using the Gaussian 09 program.[24] The calculated dipole moment is 2.723 D. The optimized structure of the complex is given in Figure S3, Supporting Information. The dissociation of one of the triphenylphosphines in the symmetrical four coordinated complex is thermodynamically favorable, and this may have happened because of the steric hindrance of the bulky triphenylphosphine ligand itself. Moreover, comparatively less stabilization energy of the unsymmetrical dimeric complex favors the mixed geometry for the complex. It is to be pointed out here that tricoordination as such is rare, and only a few such Cu(II) complexes are known.[25] To the best of our knowledge, the present work demonstrated the first example of discrete

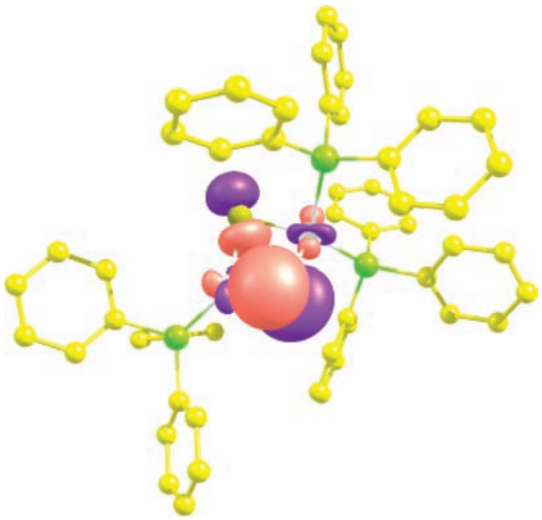


Figure 2. Highest occupied molecular orbital (HOMO) of $[(PPh_3)Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$.

unsymmetrical mixed tetrahedral and trigonal planar binuclear copper(II) complexes having two μ2-S2 units in $[(PPh_3)Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$ via the selective cleavage of the C−S bond of the thiosemicarbazone ligand. However, such a simultaneous occurrence of three- and four-coordinate Cu(I) complexes is known with the different bridging groups.[26]

An attempt was made to synthesize $[PPh_3Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$ from $[CuCl_2(PPh_3)_2]$ and elemental sulfur under refluxing conditions in ethanol− dichloromethane, which resulted in the formation of a CuS precipitate. However, the evaporation of the mother liquid afforded colorless shiny crystals. From the analytical, IR, and electronic spectra of the crystals, no appreciable information could be obtained. Hence, an X-ray crystallographic investigation was carried out. Surprisingly, it was found to be a tetranuclear cubane $[Cu_4(\mu_3\text{-}Cl)_4(PPh_3)_4]$ having triply bridged chloride ions. The structure of the complex is given in Figure 4. The well ordered (R = 0.0350) unit cell contains a tetranuclear $[Cu_4(\mu_3\text{-}Cl)_4(PPh_3)_4]$ in which Cu(1) and Cu(2) ligated with one triphenylphosphine and three of the chloride ions by forming a

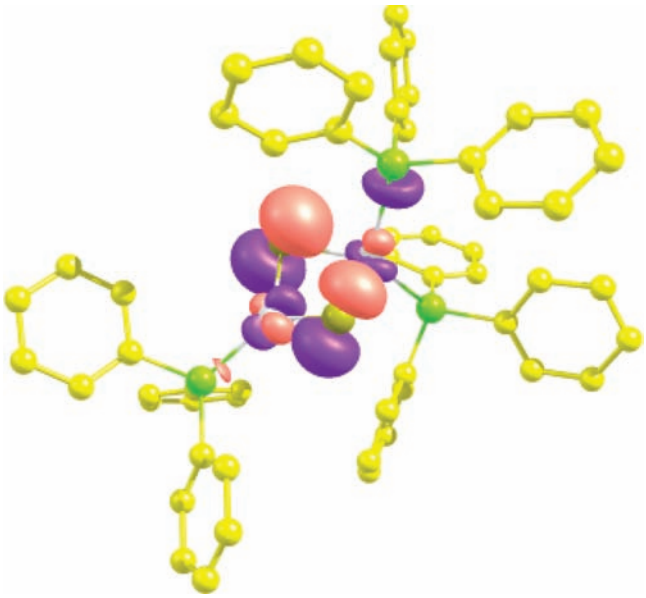


Figure 3. Lowest unoccupied molecular orbital (LUMO) of $[(PPh_3)Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$.

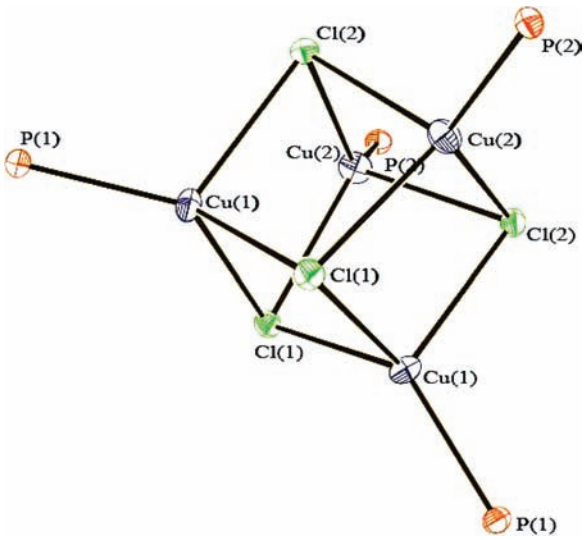


Figure 4. Structure of $[Cu_4(\mu_3\text{-}Cl)_4(PPh_3)_4]$. Phenyl rings were omitted for clarity.

tetrahedral core around each metal center. The crystallographic parameters are given in Table 3. The observed bond lengths Cu(1)−P(1) = 2.1991 Å and Cu(2)−P(2) = 2.1995 Å are less than those found in $[(PPh_3)Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$, indicating a stronger back bonding between copper and triphenylphosphine atoms (Table 4). The variation in the copper−chloride bond lengths indicates a signficant distortion in the cubane geometry.

EPR spectra of a powdered sample of $[(PPh_3)Cu(\mu\text{-}S)_2\text{-}Cu(PPh_3)_2]$ were recorded at room temperature and at liquid nitrogen temperature at the X- band frequency. No hyperfine structure was observed for the complex. The room temperature spectrum showed a broad signal with the three *g* values at 2.903, 2.717, and 2.467, indicating considerable distortion in the CuS_2P and CuS_2P_2 core (Figure 5a). However, the spectrum at 77 K (Figure 5b) showed four signals with *g* values

Table 3. Crystal Data and Structure Refinement for $[Cu_4(\mu_3\text{-}Cl)_4(PPh_3)_4]$

empirical formula	$C_{36}H_{30}Cl_2Cu_2P_2$
fw	722.52
temp	173 K
wavelength	0.71073 Å
cryst syst	orthorhombic
space group	*Pbcn*
unit cell dimensions	
a	17.428(4) Å
b	20.418(4) Å
c	18.156(4)Å
α	90°
β	90°
γ	90°
volume	6461 Å^3
Z	8
calcd density	1.486 Mg/m^3
abs coeff	16.06 mm^{-1}
F(000)	2944
cryst size	0.45 × 0.25 × 0.25 mm
θ range for data collection	1.54 to 28.27°
limiting indices	$-23 \le h \le 22$, $-27 \le k \le 27$, $-23 \le l \le 23$
reflns collected/unique	69797/6492 [R(int) = 0.0293]
completeness to θ	28.27°
absorption correction	semiempirical from equivalents
refinement method	full-matrix least-squares on F^2
data/restraints/params	7909/0/379
goodness-of-fit on F^2	0.762
final R indices [I > 2σ(I)]	R1 = 0.0350, wR2 = 0.0959
R indices (all data)	R1 = 0.0237, wR2 = 0.0839
largest diff. peak and hole	0.293 and −0.516 e.A^{-3}

3.16, 2.86, 2.42, and 2.23, indicating the distortion in the geometry around the metal ions in the binuclear complex. The appearance of four *g* values for this complex at 77 K may be attributed to the presence two different geometries around the copper centers. This has been shown in its electronic spectrum also. It could be that the first two *g* values may be due to the trigonal copper, and the remaining two *g* values may be due to the tetrahedral copper atom in the complex. A *g* value of 2.23 is indicative of a covalent nature between copper and phosphorus in the complex.[27] However, the observation of such a kind of EPR splitting pattern is not completely clear to us. The observed *g* values are higher than that observed for other sulfur bridged copper(II) complexes.[28]

The magnetic moment value of 3.9 μ_B for $[(PPh_3)Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$ showed also the paramagnetic nature of the complex corresponding to the +2 oxidation state for copper ions, having one unpaired electron each. Moreover, a Cu−S−Cu bond angle of 116.5° suggests ferromagnetic exchange in this complex. A similar behavior has already been reported for μ-OH bridged Cu(II) complexes.[29]

The ^{1}H NMR spectrum of $[Cu_4(\mu_3\text{-}Cl)_4(PPh_3)_4]$ was recorded in $CDCl_3$, and it exhibited a multiplet at 6.4−7.7 ppm is attributed to the presence of aromatic protons of the triphenylphosphine ligand (Figure S4, Supporting Information). ^{31}P NMR spectra of $[Cu_4(\mu_3\text{-}Cl)_4(PPh_3)_4]$ were recorded at room temperature and at −80 °C to determine the nature of the phousphours nuclei of triphenylphosphine. The spectrum at room temperature showed only one line at 42 ppm, which may be due to a fast exchange of triphenylphosphine ligands

dx.doi.org/10.1021/ic2022616 | *Inorg. Chem.* 2012, 51, 3525−3532

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[Cu_4(\mu_3\text{-}Cl)_4(PPh_3)_4]$

bond lengths	
Cu(1)−P(1)	2.1991(6)
Cu(1)−Cl(1)#1	2.4118(6)
Cu(1)−Cl(1)	2.4243(6)
Cu(1)−Cl(2)	2.4905(7)
Cl(1)−Cu(1)#1	2.4118(6)
Cl(1)−Cu(2)	2.4458(7)
Cu(2)−P(2)	2.1995(5)
Cu(2)−Cl(2)#1	2.3607(6)
Cu(2)−Cl(2)	2.5160(6)
Cl(2)−Cu(2)#1	2.3606(6)
bond angles	
P(1)−Cu(1)−Cl(1)#1	124.914(17)
P(1)−Cu(1)−Cl(1)	131.24(2)
Cl(1)#1−Cu(1)−Cl(1)	89.120(19)
P(1)−Cu(1)−Cl(2)	112.840(17)
Cl(1)#1−Cu(1)−Cl(2)	98.861(15)
Cl(1)−Cu(1)−Cl(2)	91.617(14)
Cu(1)#1−Cl(1)−Cu(1)	90.056(19)
Cu(1)#1−Cl(1)−Cu(2)	79.186(14)
Cu(1)−Cl(1)−Cu(2)	89.637(15)
P(2)−Cu(2)−Cl(2)#1	130.07(2)
P(2)−Cu(2)−Cl(1)	118.375(18)
Cl(2)#1−Cu(2)−Cl(1)	101.568(15)
P(2)−Cu(2)−Cl(2)	115.281(17)
Cl(2)#1−Cu(2)−Cl(2)	91.499(17)
Cl(1)−Cu(2)−Cl(2)	90.506(15)
Cu(2)#1−Cl(2)−Cu(1)	79.267(14)
Cu(2)#1−Cl(2)−Cu(2)	87.192(16)
Cu(1)−Cl(2)−Cu(2)	86.576(14)

around two copper atoms (Figure 6). Whereas, at −80 °C in addition to a singlet at 43 ppm, a very weak signal at 29 ppm was also observed. Probably at low temperatures there is some restriction on triphenylphosphine exchange, leading to the observation of two types of triphenylphosphines.

Cyclic voltammogram of the binuclear complex showed a pair of peaks on both positive and negative potentials corresponding to two successive one-electron oxidation Cu(II)−Cu(II) → Cu(III)−Cu(II) → Cu(III)−Cu(III) and similar one-electron reduction Cu(II)−Cu(II) → Cu(I)−Cu(II) → Cu(I)−Cu(I) (Figure 7).

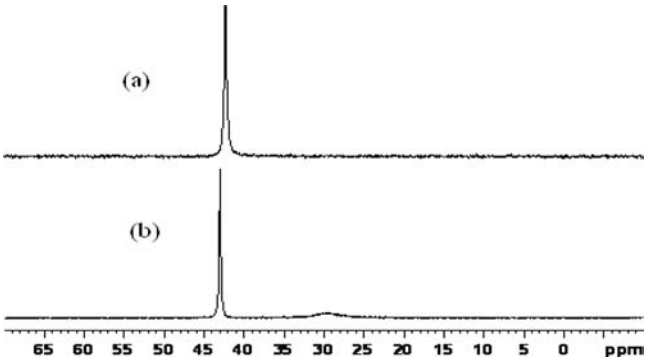


Figure 6. $^{31}\{^1H\}P$ NMR (a) at 25 °C and (b) at −80 °C in CD_2Cl_2.

The equilibrium constant K_c for comproportionation reaction in this binuclear complex is defined as

Oxidation

$$\mathrm{Cu(II)-Cu(II)} \underset{E_{1/2}(\mathrm{Oxd1})}{\overset{-e^-}{\rightleftharpoons}} \mathrm{Cu(III)-Cu(II)}$$

$$\underset{E_{1/2}(\mathrm{Oxd2})}{\overset{-e^-}{\rightleftharpoons}} \mathrm{Cu(III)-Cu(III)}$$

Reduction

$$\mathrm{Cu(II)-Cu(II)} \underset{E_{1/2}(\mathrm{Red1})}{\overset{-e^-}{\rightleftharpoons}} \mathrm{Cu(I)-Cu(II)}$$

$$\underset{E_{1/2}(\mathrm{Red2})}{\overset{-e^-}{\rightleftharpoons}} \mathrm{Cu(I)-Cu(I)}$$

$$K_c(\mathrm{II-III}) = \frac{[\mathrm{Cu(III)-Cu(II)}]^2}{[\mathrm{Cu(II)-Cu(II)}][\mathrm{Cu(III)-Cu(III)}]}$$

$$K_c(\mathrm{II-I}) = \frac{[\mathrm{Cu(I)-Cu(II)}]^2}{[\mathrm{Cu(II)-Cu(II)}][\mathrm{Cu(I)-Cu(I)}]}$$

$$K_c = e^{(F/RT)[E_{1/2}(1)-E_{1/2}(2)]}$$

The K_c value for oxidation is 9.403, and for reduction it is 9.098. These values do indicate a strong electronic coupling between the metal centers through the bridging sulfur atom. $E_{1/2}(1)$ and $E_{1/2}(2)$ are the half-wave potentials corresponding to Cu(II)−Cu(II)/Cu(III)−Cu(II) or Cu(II)−Cu(II)/Cu(I)−Cu(II) and Cu(III)−Cu(II)/Cu(III)−Cu(III) or Cu(I)−Cu(II)/Cu(I)−Cu(I).[30] The

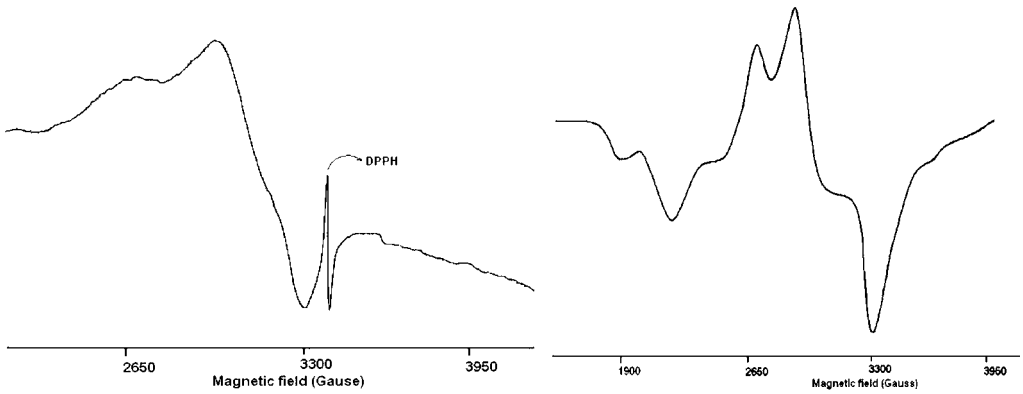


Figure 5. EPR spectrum of $[(PPh_3)Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$ at RT (a) and LNT (b).

dx.doi.org/10.1021/ic2022616 | Inorg. Chem. 2012, 51, 3525−3532

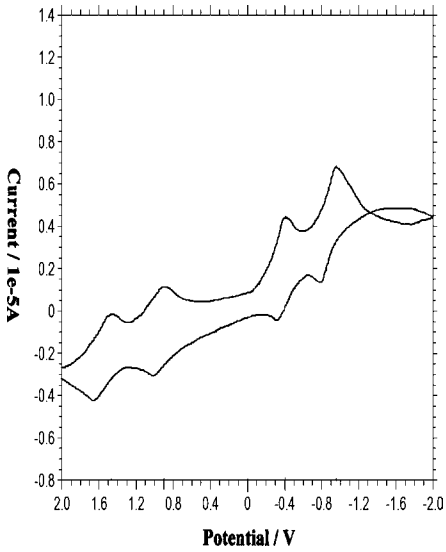


Figure 7. Cyclic voltammogram of $[(PPh_3)Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$.

high peak to peak separation values ΔEp(red) (0.07 and 0.08 V) and ΔEp(oxi) (0.2 and 0.062 V) reveal that these processes are reversible/quasi-reversible.[31] Quasi-reversibility can be attributed to either slow electron transfer or adsorption of the complexes onto the electrode surface.[32]

CONCLUSION

In this article, synthesis of $[(PPh_3)Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$ *via* the cleavage of the C−S bond of the ferrocenylthiosemicarbazone ligand has been reported. The structure of this mixed geometrical binuclear complex has been confirmed both experimentally (X-ray crystallography) and theoretically (DFT studies). In addition, a tetranuclear cubane, $[Cu_4(\mu_3\text{-}Cl)_4(PPh_3)_4]$, has been obtained while attempting to synthesize the title compound directly. A detailed study is underway on the reactions of various substituted ferrocenylthiosemicarbazones with $[CuCl_2(PPh_3)_2]$ in order to understand the mechanism for C−S bond cleavage.

ASSOCIATED CONTENT

Supporting Information

Crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledged the Council of Science and Industrial Research, New Delhi, India and Department of Science and Technology, New Delhi, India for their financial assistance. Prof. Dr. Karl Kirchner, Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria is gratefully acknowledged for his generous help in recording the NMR spectrum and for an enlightening discussion.

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(30) $[(PPh_3)Cu(\mu\text{-}S)_2Cu(PPh_3)_2]$: $E_{1/2}$(oxid.1) = 1.460 V; $E_{1/2}$(oxid.2) = 0.904 V; $E_{1/2}$(red.1) = −0.408 V; $E_{1/2}$(red. 2) = −0.946 V.
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