

Methyl Substituent at C² Carbon of Acetophenone Thiosemicarbazone Induces Unusual Heterobridging in the [(Ph₃P)Cu(μ-I)₂(μ-S-Haptsc)Cu(PPh₃)] Dimer

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The sulfur of acetophenone thiosemicarbazone {(Ph)(Me)C=N–NH–C(=S)NH₂; Haptsc} and two iodine atoms form an unusual heterobridge in the dinuclear complex [(Ph₃P)Cu(μ-I)₂(μ-S-Haptsc)Cu(PPh₃)] (1), leading to a short Cu···Cu distance of 2.504(1) Å. This uncommon heterobridging is attributed to the presence of a methyl substituent at the Schiff base C² carbon atom of the acetophenone thiosemicarbazone.

The interaction of copper with the thiosemicarbazones is of current interest from the points of view of bonding, structure, and biological aspects.^{1,2} Among nitrogen- and sulfur-donor atoms derived from the thiosemicarbazones I¹ and heterocyclic thioamides, such as pyridine-2-thione, 1,3-imidazolines, etc.,³ there is a competition between sulfur and halogen atoms for bridging two metals. This feature is common for copper(I) halides (Chart 1). For example, in copper(I) thiosemicarbazone complexes, both the halogen (mode A) and the sulfur (mode B) bridgings have been observed.⁴ In contrast, mode B is common in copper(I) complexes with the heterocyclic thioamides.⁵ Heterobridging involving both the sulfur and halogen atoms (X = Br, I, mode C) is scarce and was noted only recently with the heterocyclic thioamides.⁶

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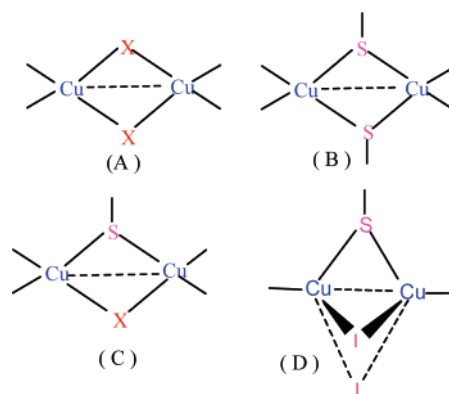
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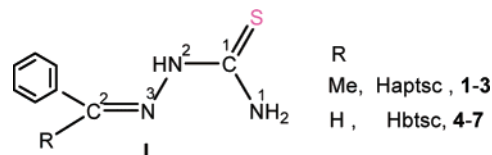
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Chart 1

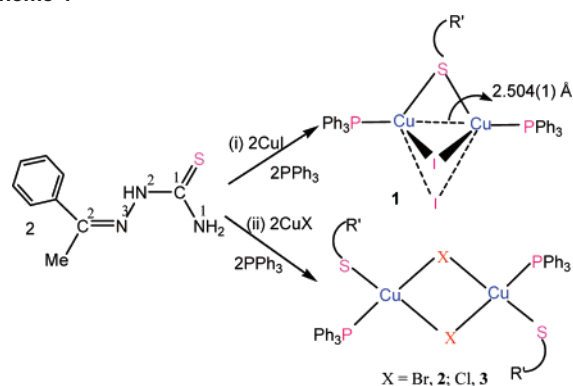


The energetic differences between the different bridging modes seem to be occasionally quite small, and the type of halogen can determine which bridging mode the complex adopts. In a reaction between a copper(I) halide (CuX) and benzaldehyde thiosemicarbazone (I, R = H) in the presence of triphenylphosphine, for example, a tetrahedral monomer, [CuI(η¹-S-Hbtsc)(PPh₃)₂]^{4a} (4), was formed for iodine, both



a monomer, [CuBr(η¹-S-Hbtsc)(PPh₃)₂]^{4a} (5), and a bromo-bridged dimer, [Cu₂(μ-Br)₂(η¹-S-Hbtsc)₂(PPh₃)₂] (6), were formed in the case of bromine, and for chlorine, a sulfur-bridged dimer, [Cu₂Cl₂(μ-S-Hbtsc)₂(PPh₃)₂]·2CH₃CN (7), was isolated.^{4a} In order to better understand this intriguing trend displayed by the Hbtsc ligand, we have investigated the bonding behavior of a closely related ligand, namely, the acetophenone thiosemicarbazone (I, R = Me) toward copper(I) in the presence of PPh₃. Reactions of the acetophenone thiosemicarbazone with copper(I) bromide or chloride in a 1:1:1 molar ratio have resulted in the formation of more common halogen-bridged dimers, [Cu₂(μ-X)₂(η¹-Haptsc)₂(PPh₃)₂] (X = Br, 2; Cl, 3) (mode A). A similar reaction

Scheme 1



with copper(I) iodide has led to the formation of a dimer with a different stoichiometry, $[\text{Cu}_2(\mu\text{-I})_2(\mu\text{-S-Haptsc})(\text{PPh}_3)_2]$ (**1**; Scheme 1).^{7,8}

Compound **1** has neither iodide bridging nor sulfur bridging alone but rather an unusual new mode of bonding involving bridging by two iodine and one sulfur atoms between two copper atoms (mode D), has been observed for the first time in metal thiosemicarbazone chemistry, and is reported in this Communication. This triple heterobridging (one sulfur and two iodine atoms) is unprecedented because all other previously reported examples of triple heterobridging involve combinations of sulfur and bromine or chlorine atoms in the complexes $[(\text{THT})\text{TaBr}_2(\mu\text{-Br})_2(\mu\text{-S-THT})\text{-TaBr}_2(\text{THT})]$ (THT = tetrahydrothiophene),⁹ $[\text{WCl}_3(\mu\text{-Sph})_2(\mu\text{-Cl})\text{WCl}_3]$,^{2-10a} and $[\text{MoO}_2(\mu\text{-Cl})(\mu\text{-SPh})_2(\text{S}_2\text{CNEt}_2)_2]^+$.^{10b}

The ^1H NMR spectrum of compound **1** in CDCl_3 (polar solvent) shows the hydrazinic ($-\text{N}^2\text{H}$) signal at δ 9.57 ppm, which is upfield relative to the similar signals in the halide-bridged dimers **2** and **3** (**2**, δ 10.37 ppm; **3**, δ 10.85 ppm). The $-\text{N}^1\text{H}_2$ group of **1** shows only one signal at δ 6.75 ppm, which is slightly upfield relative to that in compound **2** (6.81 ppm; the signal for **3** is obscured by PPh_3).⁷ Methyl

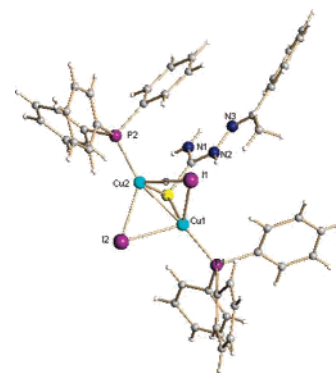


Figure 1. Molecular structure of **1** with an atomic numbering scheme.

protons show signals at 2.41, 2.37, and 2.58 ppm for **1-3**, respectively.

The ^{31}P NMR spectrum of **1** exhibits a broad signal at δ -114.3 ppm with the upfield coordination shift ($\Delta\delta$) of -1.17 ppm as compared with the coordination shifts for **2** and **3** ($\Delta\delta = 1.322$ ppm, **2**; $\Delta\delta = 1.798$ ppm, **3**). The differences in the chemical shifts point toward the different coordination modes for **1** versus **2** and **3**. The presence of a single signal in the ^{31}P NMR spectrum of **1** also indicates the stability of the structure in the solution state. In order to check the stability of sulfur bridging in **1**, an additional 1 mol of the PPh_3 donor molecule was added to its solution in the NMR cell in CDCl_3 . The NMR spectrum showed two signals, at δ -78.3 ppm ($\Delta\delta = 35.1$ ppm) and δ -110.9 ppm ($\Delta\delta = 2.2$ ppm), indicating the formation of the two new species, whose nature is not understood. However, it demonstrates the relative weakness of the sulfur bridging in **1**, as anticipated.

The findings as detailed above were corroborated by the structures of **1-3** in the solid state as determined by single-crystal X-ray diffraction. In compound **1**, two iodine and one sulfur atoms of the thiosemicarbazone ligand bridge two copper atoms, and each copper atom is further bonded to the phosphorus atom from a PPh_3 ligand. The bridging Cu-S distances [$2.393(1)$ and $2.419(1)$ Å] in **1** are longer than the terminal Cu-S distances in **2** and **3** [**2**, $2.270(2)$ Å; **3**, $2.285(1)$ Å] but are similar to those in the sulfur-bridged dimers.^{4a} However, the Cu-P bond distances in compounds **1-3** are alike [**1**, $2.199(1)$ and $2.210(1)$ Å; **2**, $2.220(2)$ Å; **3**, $2.223(1)$ Å].^{4a} The angles at the sulfur and iodine atoms [Cu-S-Cu, $62.71(3)^\circ$; Cu-I-Cu, $54.57(2)$ and $55.37(2)^\circ$] are, however, much shorter than those in the sulfur- or iodine-bridged dimers [Cu-S-Cu, $77.998(2)^\circ$,^{4a} and Cu-I-Cu, $70.72(7)^\circ$,^{4b} respectively; Figure 1]. The angular flexibility at the iodine/sulfur atoms appears to be responsible for allowing this structural change. All of the four Cu-I and I-Cu-Cu angles are different [Cu1-I1, $2.6695(7)$ Å; Cu1-I2, $2.7472(7)$ Å; Cu2-I1, $2.7873(7)$ Å; Cu2-I2, $2.6379(7)$ Å; Cu1-Cu2-I1, $60.32(2)^\circ$; Cu1-Cu2-I2, $64.53(2)^\circ$; Cu2-Cu1-I1, $65.11(2)^\circ$; Cu2-Cu1-I2, $60.10(2)^\circ$]. The angles around each Cu center lie in the range of ca. 94 – 121° , and the geometry may be formally considered as the distorted tetrahedral with two tetrahedra sharing a face comprised of one sulfur and two iodine atoms.

In compound **1**, both of the hydrogen atoms of each amino group are engaged in the intermolecular hydrogen bonding

(7) Synthesis of **1**: To a solution of copper(I) iodide (0.025 g, 0.13 mmol) in acetonitrile (15 mL) was added solid Haptsc ligand (0.025 g, 0.13 mmol), which leads to the formation of yellow precipitates after stirring for a period of 2 h. To these precipitates suspended in CH_3CN was added solid PPh_3 (0.034 g, 0.13 mmol), the resulting solution was further stirred for 1 h and filtered, and slow evaporation of the filtrate formed light-yellow crystals. Yield: 0.052 g, 69%. Mp: 215 – 217°C . Elem. anal. Calcd for $\text{C}_{45}\text{H}_{41}\text{Cu}_2\text{I}_2\text{N}_3\text{P}_2\text{S}$: C, 49.14; H, 3.73; N, 3.82. Found: C, 49.31; H, 3.99; N, 4.02. IR bands (KBr pellets, cm^{-1}): $\nu(\text{N-H})$ 3450s, 3410s, 3284m ($-\text{NH}_2$), 3198s ($-\text{NH}-$); $\nu(\text{C=N}) + \delta\text{NH}_2 + \nu(\text{C=C})$ 1583s, 1508b; $\nu(\text{C-S})$ 820s; $\nu(\text{P-C}_{\text{Ph}})$ 1093s. ^1H NMR (CDCl_3 , δ ppm): 9.57b ($-\text{N}^2\text{H}$), 6.75s ($-\text{N}^1\text{H}_2$), 7.28–7.70 m (Ph + PPh_3 + N^1H_2), 2.41s (CH_3). ^{31}P NMR (CDCl_3 , δ ppm): -114.33 , $\Delta\delta(\delta_{\text{complex}} - \delta_{\text{ligand}}) = -1.17$. ^1H and ^{31}P NMR spectra were recorded in CDCl_3 at 300.40 and 121.50 MHz frequencies on a FT-NMR AL 300 MHz JEOL spectrometer electronic absorption spectrum [CH_2Cl_2 , $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{L mol}^{-1} \text{cm}^{-1}$): 305.5 (2.49×10^4). Fluorescence spectrum: $\lambda_{\text{ex}} = 305$ nm, $\lambda_{\text{em}} = 401$ nm.

(8) Crystallographic data for **1**: $\text{C}_{45}\text{H}_{41}\text{Cu}_2\text{I}_2\text{N}_3\text{P}_2\text{S}$, $M = 1098.69$, monoclinic, $a = 8.5921(9)$ Å, $b = 21.820(3)$ Å, $c = 23.145(3)$ Å, $\alpha = 90^\circ$, $\beta = 93.483(2)^\circ$, $\gamma = 90^\circ$, $V = 4331.3(8)$ Å³, space group $P2(1)/n$; $T = 93(2)$ K, $\rho_{\text{calc}} = 1.685$ Mg m^{-3} , $Z = 4$; $\mu(\text{Mo K}\alpha) = 2.565$ mm^{-1} , 31 354 reflections measured on a CCD area detector diffractometer with graphite-monochromated Mo K α radiation and 10 497 unique reflections ($R_{\text{int}} = 0.0498$). The final $R1$ was 0.0409 for 7369 reflections [$I > 2\sigma(I)$], and $wR2$ was 0.0798.

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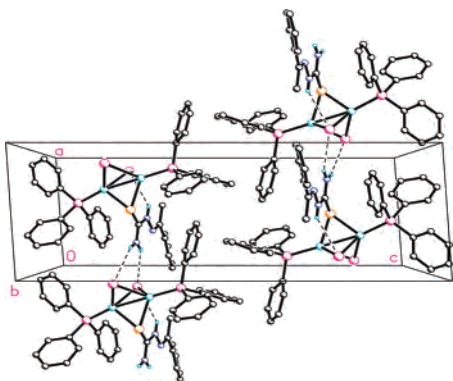


Figure 2. Packing diagram of **1**.

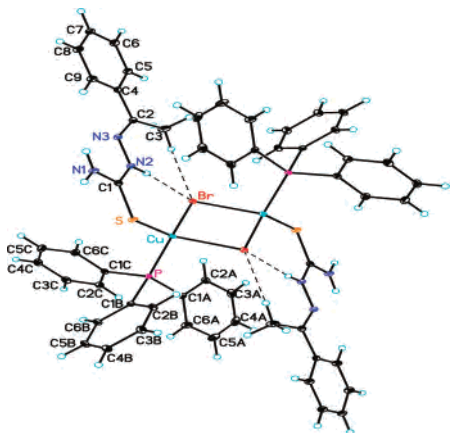
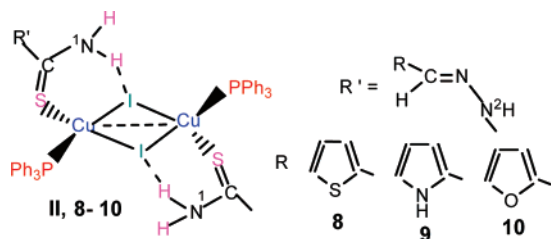


Figure 3. Molecular structure of **2**.

with the two bridging iodine atoms of a second molecule [H1B–NH1A···I1 and H1A–NH1B···I2; Figure 2]. While in the reported iodide-bridged dimers (type A), namely, $[\text{Cu}_2(\mu\text{-I})_2(\text{Httsc})_2(\text{PPh}_3)_2]$ (**8**), $[\text{Cu}_2(\mu\text{-I})_2(\text{Hptsc})_2(\text{PPh}_3)_2]$ (**9**), and $[\text{Cu}_2(\mu\text{-I})_2(\text{Hftsc})_2(\text{PPh}_3)_2]$ (**10**), only one hydrogen atom of each amino group forms one intramolecular hydrogen bond with a bridging iodine atom; the second hydrogen atom is not hydrogen-bonded (**II**).⁴



The amino groups in compounds **2** and **3** (Scheme 1) are not involved in the hydrogen bonding, similar to that in **1**. Rather, one hydrogen of the amino group is engaged in the intermolecular $-\text{N}^1\text{H}\cdots\text{S}$ bonding, and the second hydrogen is nonbonded. It will be interesting to point out here that the bridging halogen atoms in **2** and **3** form the intramolecular hydrogen bonds with the imino ($-\text{N}^2\text{H}$) and methyl hydrogen atoms [$-\text{N}^2\text{H}\cdots\text{X}$ and $\text{CH}_2\text{H}\cdots\text{X}$, X = Br, **2**; Cl, **3**; Figure 3]. Compound **1** has similar intramolecular imino ($-\text{N}^2\text{H}$)–iodine hydrogen bonding, but there is no similar methyl–halogen hydrogen bonding, and this group becomes free, which appears to orient its amino group in such a way that it makes it more suitable to engage in the intermolecular

hydrogen bonding with the iodine atoms as detailed above. The simultaneous imino and methyl hydrogen bonding appears to have favored halogen bridging in **2** and **3**, similar to compound **6**, unlike the sulfur bridging in compound **7**.^{4a}

Another interesting feature of the structure of complex **1** is the short Cu–Cu distance of 2.504(1) Å, which is comparable to the Cu–Cu distance (2.5 Å) in the Cu_A center in cytochrome *c* oxidase¹¹ but much shorter than those in **2** and **3** [**2**, 3.199(2) Å; **3**, 3.1622(4) Å]. The latter distances are more comparable with the literature values for the iodide- or sulfur-bridged dimers (ca. 2.81–3.24 Å).^{4a} Complexes with short Cu–Cu distances are known to display properties such as fluorescence and phosphorescence.¹² Interestingly, the solution of complex **1** in CH_2Cl_2 also showed a weak fluorescence band at $\lambda = 401$ nm upon excitation with the radiation of $\lambda = 305.5$ nm, while compounds **2** and **3** did not show similar behavior (the free ligand is not fluorescent).

In conclusion, the ligand Hbtsc (**I**, R = H) has formed monomers and dimers (**4**–**7**), while the Haptsc ligand (**I**, R = Me) has formed only dimers (**1**–**3**), with the differences as noted above. The apparent difference in the bonding and nuclearity of the compounds formed by the two ligands is attributed to the presence of the methyl substituent at the C^2 carbon atom in the acetophenone thiosemicarbazone (Haptsc). This group appears to have a dual role: the first altering the nature of the intra- or intermolecular hydrogen bonding and the second offering steric hindrance. It may be worth pointing out here that, for X = iodide, the Haptsc ligand did not form a monomer similar to **4**, from a 1:1:2 molar ratio, but rather a known cubane $\text{Cu}_4\text{I}_4(\text{PPh}_3)_4$ was formed. Further, it appears that the expected iodide-bridged dimer, $[\text{Cu}_2(\mu\text{-I})_2(\eta^1\text{-S-Haptsc})_2(\text{PPh}_3)_2]$ similar to **2** or **3**, appears to be less stable because of the steric crowding caused by the bulky Haptsc and PPh_3 ligands in terminal positions and bulky iodine atoms connecting two copper atoms. This steric crowding appears to have favored only one Haptsc ligand bridging two copper atoms via its sulfur atom in **1**. Iodide-bridged dimers **8**–**10** have less steric compulsions because of the different substituents at the C^2 carbon.

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Supporting Information Available: X-ray crystal data in CIF format (CCDC numbers are 623690 for **1**, 623691 for **2**, and 623692 for **3** and are available upon request from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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