Dalton Transactions

Cite this: Dalton Trans., 2012, 41, 4845



2-Benzoylpyridine thiosemicarbazone as a novel reagent for the single pot synthesis of dinuclear Cu^{I} - Cu^{II} complexes: formation of stable copper(II)-iodide bonds⁺

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Received 11th January 2012, Accepted 6th February 2012 DOI: 10.1039/c2dt30068k

2-Benzoylpyridine thiosemicarbazone $\{R^1R^2C^2=N^2\cdot N^3H-C^1(=S)-N^4H_2, R^1=py-N^1, R^2=Ph\}$ Hbpytsc} with copper(1) iodide in acetonitrile-dichloromethane mixture has formed stable Cu^{II} -I bonds in a dark green Cu^{II} iodo-bridged dimer, $[Cu_2^{II}(\mu-I)_2(\eta^3-N^1,N^2,S-bpytsc)_2]$ 1. Copper(I) bromide also formed similar Cu^{II}–Br bonds in a dark green Cu^{II} bromo-bridged dimer, [Cu₂^{II}(µ-Br)₂(η³-N¹,N²,Sbpytsc)₂] **3**. The formation of dimers **1** and **3** appears to be due to a proton coupled electron transfer (PCET) process wherein copper(I) loses an electron to form copper(II), and this is accompanied by a loss of $-N^{3}H$ proton of Hbpytsc ligand resulting in the formation of anionic bpytsc⁻. When copper(1) iodide was reacted with triphenylphosphine (PPh₃) in acetonitrile followed by the addition of 2-benzoylpyridine thiosemicarbazone in dichloromethane (Cu : PPh₃ : Hbpytsc in the molar ratio 1 : 1 : 1), both Cu^{II} dimer 1 and an orange Cu^{I} sulfur-bridged dimer, $[Cu_{2}^{I}I_{2}(\mu-S-Hbpytsc)_{2}(PPh_{3})_{2}]$ 2 were formed. Copper(1) bromide with PPh₃ and Hbpytsc also formed Cu^{II} dimer 3 and an orange Cu^I sulfur-bridged dimer, $[Cu_2^{I}Br_2(\mu-S-Hbpytsc)_2(PPh_3)_2]$ 4. While complexes 2 and 4 exist as sulfur-bridged Cu^I dimers, 1 and 3 are halogen-bridged. The central Cu_2S_2 cores of 2 and 4 as well as Cu_2X_2 of 1 (X = I) and 3 (X = Br) are parallelograms. One set of Cu^{II}–I and Cu^{II}–Br bonds are short, while the second set is very long {1, Cu–I, 2.565(1), 3.313(1) Å; 3, Cu-Br, 2.391(1), 3.111(1) Å}. The Cu-Cu separations are long in all four complexes {1, 4.126(1); 2, 3.857(1); 3, 3.227(1); 4, 3.285(1) Å}, more than twice the van der Waals radius of a Cu atom, 2.80 Å. The pyridyl group appears to be necessary for stabilizing the Cu^{II}-I bond, as this group can accept π -electrons from the metal.

Introduction

The stabilization of copper(II)–iodide bonding has been enigmatic owing to the reducing nature of the bulky iodide anion. It generally appears outside the coordination sphere, as exemplified by copper(II) complexes, [CuL]I {L = 2(2-aminoethyl)pyridine},¹ [CuClL₂]I {L = 1,10-phenanthroline},² and [CuLL'₂]I {L = 4-methylbenzoic acid, L' = 2,2'-bipyridine}.³ However, in the literature, polydentate N-donor ligands have been used for the formation of copper(II)–iodide bonds with distances of 2.56–2.74 Å.^{4,5} In one case with a chiral N-donor ligand, a short Cu^{II}–I distance (2.337 Å) has also been reported.⁶

Recently from this laboratory, coordination chemistry of thiosemicarbazones, an important class of thio-ligands, $\{R^1R^2C^2=$ N–NH–C¹(=S)NR³R⁴}, has been reported.⁷ The substituents at the C² atoms of neutral thiosemicarbazones were found to affect the nuclearity and nature of bonding of complexes of copper(1) halides, forming mono-, di- and poly-nuclear copper(1) complexes.⁷ These complexes of copper(1) halides with neutral thiosemicarbazones could usually be crystallized in the presence of triphenyl phosphine as a co-ligand, $^{7b-i,k,l}$ and only in a few cases crystalline products were formed in the absence of triphenyl phosphine.^{7j,m} Further, in all these cases, the thio-ligands coordinated to Cu^I as neutral ligands either in η^1 -S or μ -S modes.^{7b-m}

It was noted in the reactions of copper(i) iodide with thiosemicarbazones (Htsc) that the variation of R^1 and R^2 substituents at the C^2 carbon gave different products (Chart 1). For the substituents, Ph, H and py, H, mononuclear, [CuI(Htsc)(PPh_3)₂],^{7b} for Ph, Me dinuclear, [(Ph_3P)Cu(µ-I)₂(µ-S-Htsc)Cu(PPh_3)]⁷¹ and Ph, Ph combination, three coordinate mononuclear,



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[†]CCDC reference numbers 710209–710212 for complexes 1–4. For crystallographic data in CIF or other electronic format see DOI: 10.1039/ c2dt30068k

 $[CuI(\eta^1-S-Htsc)_2]^{7j}$ complexes were formed. In our curiosity to observe the effect of Ph, py substituents at C² carbons, we have come across unusual coordination behaviour of 2-benzoylpyridine thiosemicarbazone (Hbpytsc, R¹, R² = Ph, py) during equimolar reactions with copper(1) iodide/bromide in the presence and absence of triphenyl phosphine. The formation of the halogen-bridged Cu^{II} dinuclear complexes (1, 3) in the presence of Ph₃P along with the sulfur-bridged Cu^I dinuclear complexes (2, 4) and the novelty of 2-benzoylpyridine thiosemicarbazone to stabilize formation of copper(II)–iodide bonds are described herein.

Experimental section

General materials and techniques

Copper(I) halides were prepared by reducing an aqueous solution of $CuSO_4 \cdot 5H_2O$ using SO_2 in the presence of NaX (X = Cl, Br, I) in water.⁸ The ligand 2-benzoylpyridine thiosemicarbazone was prepared by refluxing thiosemicarbazide with 2-benzoylpyridine in presence of acetic acid in methanol for a period of 24 h. The elemental general analyses (C, H and N) were obtained using a Thermoelectron FLASHEA1112 CHNS analyzer. The IR spectra were recorded using KBr pellets in the range 4000-200 cm⁻¹ on a FTIR-SHIMADZU 8400 Fourier transform spectrophotometer and on a Pye-Unicam SP-3-300 spectrophotometer. The UV-visible spectroscopy was done using a SHIMADZU UV-1601PC spectrophotometer. ESR studies were carried out using an X-band spectrometer. The melting points were determined with a Gallenkamp electrically heated apparatus. ¹H NMR spectra were recorded on a JEOL AL-300 FT spectrometer operating at a frequency of 300 MHz in CHCl₃-d with TMS as the internal reference. Cyclic voltammograms were recorded on an Autolab Electrochemical System equipped with PGSTAT20 apparatus driven by GPES software employing a platinum working electrode and an SCE reference electrode. All solutions were 10^{-3} mmol L⁻¹, and the supporting electrolyte was 10^{-1} mmol L⁻¹ of tetraethyl ammonium perchlorate.

$[Cu_{2}^{II}I_{2}(\eta^{3}-N^{1},N^{2},S-bpytsc)_{2}]\cdot 2CH_{3}CN$ (1)

PPh₃ (0.045 g, 0.17 mmol) was added to a solution of copper(1) iodide (0.025 g, 0.17 mmol) in CH₃CN, followed by stirring for 1 h resulting in formation of a white precipitate. Solid Hbpytsc ligand (0.031 g, 0.17 mmol) and CH₂Cl₂ (5 mL) were added to these precipitates in CH₃CN, followed by refluxing for 10 min resulting in a clear dark orange colored solution, which on slow evaporation yielded dark green crystals of $[Cu_2^{II}I_2(\eta^3-N^1,N^2,$ S-bpytsc)₂ (1) along with orange crystals of $[Cu_2I_2(\mu-S Hbpytsc)_2(PPh_3)_2$ (2). The crystals were manually separated and characterized. The direct reaction of copper(1) iodide with Hbpytsc in CH₃CN-CH₂Cl₂ was also carried out which essentially gave complex 1 with an enhanced yield of 75%. Data for 1, yield, 0.011 g, 38%; mp. 200-202 °C). Anal. Calcd for $C_{26}H_{22}Cu_2I_2N_8S_2$ ·2CH₃CN: C, 37.00; H, 2.88; N, 14.39%. Found: C, 36.88; H, 2.75; N, 13.93%. Main IR peaks (KBr, cm^{-1}): v(N-H) 3269s (-NH₂); v(C-H) 3096s, 3055s; v(C=N) + $\delta NH_2 + \nu (C=C)$ 1622s, 1583s, 1480s; $\nu (C-N)$ 1056s, 1107s; v(C–S) 779s, 733s. Electronic absorption spectra [CH₃OH, λ_{max}

($\varepsilon \ L^{-1} \ mol^{-1} \ cm^{-1}$)]: 296 (1.07 × 10⁴), 416.5 (0.6776 × 10⁴). X-band ESR signals: $g_{\parallel} = 3.85$ and $g_{\perp} = 2.05$. This complex is partially soluble in CHCl₃ and soluble in hot CH₃OH. Data for **2** is given below.

[Cu₂I₂(µ-S-Hbpytsc)₂(PPh₃)₂]·CH₂Cl₂ (2)

Yield: orange, 0.017 g , 42%. Mp: 225–227 °C. Anal. Calcd for $C_{62}H_{54}Br_2Cu_2N_8S_2P_2\cdot CH_2Cl_2$: C, 53.69; H, 4.00; N, 7.95%. Found: C, 53.40; H, 4.21; N, 7.89%. Main IR peaks (KBr, cm⁻¹): v(N-H) 3485m, 3418s, 3203b (–NH₂) 3121b (–NH–); $v(C=N) + \delta(N-H) + v(C=C)$ 1597s, 1506s; v(C-N) 1107s, 1049s, 1026s; v(P-CPh) 1095s; v(C=S) 833s (thioamide moiety). ¹H NMR (CDCl₃, δ , ppm) 7.23–7.51 m (PPh₃ + Ph + C⁴H + N¹H₂),7.74 (td, C⁵, ⁶H), 8.82d (C⁷H), 9.45sb (N¹H₂), 14.09s (–N²H–). Electronic absorption spectra [CH₂Cl₂, λ_{max} ($\varepsilon L^{-1} \text{ mol}^{-1} \text{ cm}^{-1}$)]: 355 (0.168 × 10⁴).

[Cu2^{II}Br2(η³-N¹, N², S-bpytsc)2]·2CH3CN (3)

PPh₃ (0.045 g, 0.17 mmol) was added to a solution of copper(1) bromide (0.025 g, 0.17 mmol) in CH₃CN, followed by stirring for 1 h resulting in formation of a white precipitate. Solid Hbpytsc ligand (0.031 g, 0.17 mmol) and CH₂Cl₂ (5 mL) were added to it, followed by refluxing for 10 min resulting in a clear dark orange solution, which on slow evaporation of the solution yielded dark green crystals of $[Cu^{II}Br(\eta^3-N^1,N^2,S-bpytsc)]$ (3) and orange crystals of $[Cu_2Br_2(\mu-S-Hbpytsc)_2(PPh_3)_2]$ (4). Data for 3, yield, 014 g, 38%; mp. 205-207 °C. Anal. Calcd for C₂₆H₂₂Cu₂Br₂N₈S₂·2CH₃CN: C, 40.96; H, 3.19; N, 15.93%. Found: C, 40.78; H, 4.24; N, 16.09%. Main IR peaks (KBr, cm⁻¹): v(N-H) 3439s, 3271s (-NH₂); v(C-H) 3081s, 3047s; $v(C=N) + \delta(N-H) + v(C=C)$ 1601s, 1481s, 1433s; v(C-N)1118s, 1105s, 925s; v(C-S) 781s, 731s. Complex is partially soluble in hot CH₃OH and insoluble in CH₃CN. Electronic absorption spectra [CH₃OH, λ_{max} ($\varepsilon L^{-1} mol^{-1} cm^{-1}$)]: 296 (1.88×10^4) , 417 (1.16×10^4) . X-band ESR signals: $g_{\parallel} = 3.75$ and $g_{\perp} = 2.07$. Data for **4** is given below.

[Cu₂Br₂(µ-S-Hbpytsc)₂(PPh₃)₂] (4)

Yield: orange, 0.026 g, 47%. Mp: 218–220 °C. Anal. Calcd for $C_{62}H_{54}Cu_2I_2N_8P_2S_2$: C, 52.51; H, 3.81; N, 7.90%. Found: C, 52.84; H, 4.10; N, 7.98%. Main IR peaks (KBr, cm⁻¹): v(N-H) 3419s, 3225m (–NH₂) 3126s (–NH–); $v(C=N) + \delta NH_2 + v(C=C)$ 1597s, 1585s, 1506s; v(C=S) 833s (thioamide moiety); v(C-N) 1100s, 1050s; $v(P-C_{Ph})$ 1095s. ¹H NMR (CDCI₃, δ ppm) 7.29–7.61 m (PPh₃ + Ph + C⁴H + N¹H₂), 7.78 (td, C⁵, ⁶H), 8.95d (C⁷H), 14.03s (–N²H). Electronic absorption spectra [CH₂Cl₂, λ_{max} (εL^{-1} mol⁻¹ cm⁻¹]: 343 (0.176 × 10⁴).

X-ray crystallography

The data for compounds 1 and 3 was measured on a Bruker AXS SMART APEX CCD diffractometer with graphite monochromated Mo-K α radiation at 100(2) K. Single crystals of 2 and 4 were mounted on an Oxford Diffraction Gemini diffractometer equipped with graphite monochromated Mo-K α radiation

 $(\lambda = 0.71073 \text{ Å})$ and the unit cell dimensions and intensity data were measured at 200(2) K (2) and 296(2) K (4). The structure was solved by direct methods using the program SHELXS-97 (1, 2, 4), SHELXTL 6.14 (3) and refined by full-matrix leastsquares techniques against F^2 using SHELXL-97.¹⁴ Positional and anisotropic atomic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms bonded to carbon were placed geometrically and the N-H hydrogen atoms were initially positioned at sites determined from difference maps, but the positional parameters of all H atoms were included as fixed contributions riding on attached atoms with isotropic thermal parameters 1.2 times those of their carrier atoms. Criteria for a satisfactory complete analysis were the ratio of rms shift to standard deviation being less than 0.001, and there being no significant features in the final difference maps. Scattering factors from the International Tables for X-ray crystallography were used.⁹

Results and discussion

Synthesis

Scheme 1 shows the formation of complexes 1-4. Copper(1) iodide with PPh₃ in CH₃CN formed a white solid which was further reacted with 2-benzoylpyridine thiosemicarbazone (Hbpytsc) in CH₂Cl₂. A slow evaporation of the mixture yielded two products: a dark green copper(II) compound, $[Cu_2^{II}(\mu-I)_2(\eta^3 N^1$, N^2 , S-bpytsc)₂ 1, and an orange copper(I) compound, $[Cu_2^{I}I_2(\mu-S-Hbpytsc)_2(PPh_3)_2]$ **2**. However, the direct reaction of copper(I) iodide with Hbpytsc in CH₃CN-CH₂Cl₂ mixture in the absence of Ph₃P formed only dark green complex 1 (Scheme 1). The behaviour of copper(1) bromide in the presence and absence of Ph₃P was similar to that of copper(I) iodide. It formed a dark green Cu^{II} complex, $[Cu_2^{II}(\mu-Br)_2(\eta^3-N^1, N^2, S-bpytsc)_2]$ 3 and an orange Cu^{I} dimer, $[Cu_{2}^{I}Br_{2}(\mu-S-Hbpytsc)_{2}(PPh_{3})_{2}]$ 4. It is important to point out that in the literature, reactions of copper(I) halides with the thio-ligands in the presence of tertiary phosphines invariably have yielded copper(1) complexes, several of which are similar to **2** and **4**.⁷ The formation of Cu^{II} complexes (**1** and **3**) using 2-benzoylpyridine thiosemicarbazone in the presence of Ph₃P along with Cu^I complexes (**2** and **4**) under reducing conditions demonstrates the novelty of this thio-ligand to stabilize copper(II)–halogen bonds, particularly the stabilization of copper(II)–iodide bonds, whose occurrence in the literature is limited^{4–6} and rare among the thio-ligands.^{10*a*} The use of excess PPh₃ merely formed the usual mononuclear tetrahedral Cu^I complexes, [Cu^IX(η¹-S-Hbpytsc)(PPh₃)₂] (X = Cl, Br).^{7*a*,10*b*} With copper(I) chloride and bromide, a related thio-ligand, namely, benzophenone thiosemicarbazone (Hbztsc) (Ph, Ph substituent at C² carbon) formed monomeric tetrahedral complexes, [CuX(Hbztsc)(PPh₃)₂] (X = Cl, Br) and with copper(I) iodide, it formed a trigonal planar complex, [CuI(Hbztsc)₂].^{7*j*}

Spectroscopy, magnetism and electrochemistry

IR spectroscopy of the complexes has confirmed the presence of the individual ligands through their v(N-H), $v(C-H)_{Me}$, v(C-N), v(C=C), v(C=N), v(O-H) and v(P-C) vibrational modes. The ¹H NMR spectra of complexes 1 and 3 showed the absence of a diagnostic imino proton signal (-N³H), and it revealed that Hbpytsc is anionic in these complexes. However, Cu^I dimers 2 and 4 showed signals due to various groups including that due to $-N^{3}H$ protons and it confirmed that the ligand Hbpytsc is neutral in these complexes (see the Experimental section). The divalent state of copper in dinuclear complexes 1 and 3 is confirmed by measuring their magnetic susceptibility which yielded the magnetic moments 1.77 and 1.76 B. M. respectively. Complex 1 showed a very broad but symmetrical ESR spectrum with a g value centered at 2.05. There is partial resolution of the coupling from the Cu nucleus (I = 3/2) and thus a weak signal at 3.85 could be attributed to $g_{\parallel} = 3.85$ and in that case $g_{\perp} = 2.05$. This ESR datum supports a distorted square pyramidal environment around the Cu atom (Fig. 1). Complex 3 showed a similar ESR spectrum. The electronic absorption spectrum of complex 1 in methanol (Fig. 2) showed two bands, one broad band at 296 nm





Fig. 1 EPR spectrum of complex 1 at 120 K.



Fig. 2 Electronic absorption spectrum of complex 1.



Fig. 3 Cyclic voltammogram of complexes 1 and 3 at a scan rate of 0.05 V $\rm s^{-1}.$

(due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions) and a second at 417 nm, attributed to the S \rightarrow Cu^{II} LMCT transition characteristic of divalent copper(II)–sulfur bonds;¹¹ complex **3** showed a similar spectrum. The electronic absorption spectra of Cu^I complexes **2** and **4** each showed a single weak band at 343 and 355 nm, respectively. The cyclic voltammogram (CV) of complex **1** displayed a quasi-reversible Cu^{II}–Cu^{III} redox couple at $E_{\frac{1}{2}} = 0.813$ V with a peak-to-peak separation (ΔE_p) of 102 mV (Fig. 3). The CV of complex **3** displays an irreversible Cu^{II}–Cu^{III} redox couple with $E_{\frac{1}{2}}$ value of 0.794 V (ΔE_p , 120 mV). The Cu^{II}–Cu^{III} redox couples of **1** and **3** are higher than in the literature reports¹² and appear to be responsible for the stabilization of copper(II)–iodide bonding. The pyridyl group appears to be necessary for stabilizing the Cu^{II} –I bond, as this group can accept π -electrons from the metal.

Crystal and molecular structures

The crystal data are given in Table 1 and the bond parameters are given in Table 2. Complex 1 is a centrosymmetric dimer, $[Cu_2^{II}(\mu-I)_2(\eta^3-N^1,N^2,S-bpytsc)_2]$ with each Cu^{II} bonded to N¹, N^2 , S-donor atoms of a tridentate anionic bpytsc⁻ ligand (Fig. 4) (Table 2). Each Cu is further bonded to two bridging iodide ions with one short Cu^{II}-I bond, 2.5651(6) Å and one long Cu^{II}-I bond, 3.3129(6) Å (Scheme 1). The short Cu^{II}–I bond distance is comparable to the 2.56-2.74 Å observed with N-donor ligands,^{4,5} and is somewhat shorter than the 2.601(1) Å observed in a sulfur bridged dimer.¹⁰ The geometry around each metal center can be described as distorted square pyramid with the long Cu-I bond occupying the axial position. The atoms, N(1), N(2), S(1) and I(1) form the square plane with non linear trans bond angles, N(2)-Cu(1)-I(1), 179.54(10)°; N(1)-Cu(1)-S(1), 164.68(10)° suggesting distortion in the geometry. Dimer $[Cu_2^{II}Br_2(\eta^3-N^1, N^2, S-bpytsc)_2]$ (3) showed similar bonding and structure with one short and one long Cu^{II}-Br bond {2.391(1), 3.111(1) Å} (Fig. 5). The long Cu(1)-Br(1) bond occupies the axial position with similar trans bond angles, N(2)-Cu(1)-Br(1), 179.32(5)°; N(1)-Cu(1)-S(1), 164.51(5)°. Complexes 2 and 4 exist as sulfur-bridged Cu^I dimers, [Cu₂X₂(µ-S-Hbpytsc)₂(PPh₃)₂] (X; I 2; Br 4.) Each copper atom is bonded to one halogen atom, one P atom from the PPh3 ligand and two S atoms of the two neutral Hbpytsc ligands (Fig. 6 and 7). The central Cu₂S₂ cores are parallelograms in thees two cases due to unequal Cu-S bond distances. The bond parameters and structures are similar to dinuclear copper(1) halide complexes with thiosemicarbazones reported in the literature.7b,c The Cu--Cu separations are long in all the four complexes $\{1, 4.126(1); 2, 4.126(1); 4.126(1); 4.126(1);$ 3.857(1); 3, 3.227(1); 4, 3.285(1) Å}, more than twice the van der Waals radius of a Cu atom, 2.80 Å.¹³

Packing interactions

Complexes 1 and 3 do not involve intramolecular interactions, however, in each case the amino hydrogen of one dimer interacts with the N³ atom and the phenyl group of an adjacent dimeric unit along the *a*-axis and *vice versa* { $N^{4}H\cdots N^{3}$, $N^{4}H\cdots \pi(ph)$: 1, 2.130, 2.890 Å, 2.126, 2.892 Å 3} forming 1D chains. These 1D chains interact with one another via I...H(ph) 3.01 Å (1) or Br...H(ph), 2.87 Å (3) along the *b*-axis and form 2D sheets (Fig. 8). In complexes 2 and 4, hydrazinic hydrogens (N³H) exhibit short intramolecular interactions with pyridyl nitrogen, $N^{3}H\cdots N^{1}(py)$ (1.91, 2; 1.92 Å 4). The sulfur-bridged dimers interact with one another along the a-axis via the pyridyl-phenyl moieties {C-H_(pv)··· π (Ph-P): **2**, 2.80, **4**, 2.81 Å} forming 1D chains. These chains interact with one another through a phenyl-phenyl interaction involving PPh₃ and thio-ligands $\{C-H_{(Ph-P)}\cdots\pi_{(Ph at C2)}: 2, 2.324; 4, 2.321 \text{ Å}\}$ and form 2D sheets (Fig. 9).

Mechanism

The formation of complex **1** appears to be due to a proton coupled electron transfer (PCET) process wherein copper(i) loses

 Table 1
 Crystallographic data for complexes 1–4

	1	2	3	4
Formula	C26H22Cu2I2N8S2	C ₆₂ H ₅₄ Cu ₂ I ₂ N ₈ P ₂ S ₂	C ₂₆ H ₂₂ Br ₂ Cu ₂ N ₈ S ₂	$C_{62}H_{54}Br_2Cu_2N_8P_2S_2$
Mol. weight (amu)	891.56	1418.07	797.54	1324.09
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	C2/c	$P\overline{1}$	C2/c	$P\bar{1}$
a (Å)	11.196(1)	11.7052(6)	10.9775(12)	11.8176(18)
$b(\mathbf{A})$	22.689(3)	12.3415(4)	22.299(2)	12.2666(17)
$c(\dot{A})$	11.979(2)	13.1671(5)	11.9300(13)	12.9683(19)
α (°)		62.760(4)		61.805(15)
$\beta(\circ)$	104.885(2)°	64.620(4)	106.245(2)	65.714(14)
γ (°)		67.984(4)		67.653(14)
$V(Å^3)$	2940.8(6)	1489.66(11)	2803.8(5)	1469.2(4)
Z	4	1	4	1
$T(\mathbf{K})$	100(2)	200(2)	100(2)	296(2)
ρ_{calcd} (g cm ⁻³)	2.014	1.581	1.889	1.497
$\mu (\text{mm}^{-1})$	3.721	1.920	4.550	2.256
Absolute reflec.	11154	22101	14150	24020
Unique, R_{int}	3637, 0.0278	9728, 0.0390	3499, 0.0236	9721, 0.0524
Reflec. with $I > 2\sigma(I)$	3140	6047	3053	4085
R	0.0343	0.0382	0.0237	0.0336
wR	0. 0871	0.0758	0.0559	0.0546

 Table 2
 Bond distances (Å) and bond angles (°) for complexes 1–4

Complex 1			
Cu(1)–N(2)	1.990(3)	Cu(1)–I(1)	2.5650(6)
Cu(1)-N(1)	2.009(3)	Cu(1)-S(1)	2.2292(11)
Cu–Cu	4.126(1)		
N(1)-Cu(1)-S(1)	164.68(10)	N(2)-Cu(1)-S(1)	84.35(9)
N(2)-Cu(1)-I(1)	179.54(10)	N(1)-Cu(1)-I(1)	99.42(10)
N(2)-Cu(1)-N(1)	80.82(13)	S(1)-Cu(1)-I(1)	95.44(3)
Complex 3			
Cu(1) - N(1)	1.9984(17)	Cu(1)– $Br(1)$	2.3906(4)
Cu(1) - N(2)	1.9851(16)	Cu(1)-S(1)	2.2258(6)
Cu–Cu	3.227(1)		
N(2)-Cu(1)-Br(1)	179.32(5)	N(2)-Cu(1)-S(1)	84.40(5)
N(1)-Cu(1)-S(1)	164.51(5)	N(1)-Cu(1)-Br(1)	98.97(5)
N(2)-Cu(1)-N(1)	80.67(6)	S(1)-Cu(1)-Br(1)	95.912(16)
Complex 2			
Cu–Cu	3.857(1)	Cu–S	2.4298(7)
Cu–P	2.2506(7)	Cu–S*	2.3644(7)
Cu–I	2.5847(4)	S-Cu-I*	115.776(19)
P-Cu-S	117.93(3)	S-Cu-I	106.10(2)
P-Cu-S*	105.27(3)	Cu–S–Cu*	83.20(2)
PCuI	114.08(2)	S-Cu-S*	96.80(2)
Complex 4			
Cu–Cu	3.285(1)	Cu–S	2.4622(8)
Cu–P	2.2454(8)	Cu–S*	2.3716(7)
Cu–Br	2.4152(6)	P-Cu-S*	106.58(2)
PCuS	117.44(3)	BrCuS	106.79(2)
P–Cu–Br	116.47(3)	Cu–S–Cu*	85.56(2)
S*–Cu–Br	113.79(2)	S-Cu-S*	94.44(3)



Fig. 4 Molecular structure of $[Cu_2^{II}(\mu-I)_2((\eta^3-N^1, N^2, S-bpytsc)_2]$ (1).



Fig. 5 Molecular structure of $[Cu_2^{II}(\mu-Br)_2(\eta^3-N^1, N^2, S-bpytsc)_2]$ (3).

Conclusions

In conclusion, the presence of both phenyl and pyridyl substituents at the C² group {Ph(py-N¹)C²=N²-N³H-C¹(=S)-N⁴H₂} has imparted an unusual property to 2-benzoylpyridine thiosemicarbazone, that of stabilizing Cu^{II}-halogen bonds in presence of reducing conditions such as presence of a tertiary phosphine, Ph₃P and a thio-ligand. Significantly, this thio-ligand acts as a

an electron to form copper(II), and this is accompanied by the loss of a $-N^{3}H$ proton from the Hbpytsc ligand resulting in the formation of anionic bpytsc⁻ (Scheme 2). It appears that this proton captures the electron lost by the copper(I) to form a H atom, which may have recombined with another H atom moiety to probably form H₂, but this could not be proved by experimental procedures. The pyridyl group appears to be necessary for stabilizing the Cu^{II}–I bond, as this group can accept π -electrons from the metal. A similar mechanism is suggested for the formation of complex **3**.



Fig. 6 Molecular structure of [Cu₂I₂(µ-S-Hbpytsc)₂(PPh₃)₂] (2).



Fig. 7 Molecular structure of [Cu₂Br₂(µ-S-Hbpytsc)₂(PPh₃)₂] (4).



Fig. 8 Packing diagram of dimer 1 showing the 2D sheet (dimer 3 has similar packing).

novel reagent to stabilize rare copper(II)-iodide bonds. Thiosemicarbazones with various other substituents at C² have formed mono-, di- and poly-nuclear copper(I) complexes.⁷ Pyridine-2carbaldehyde thiosemicarbazone having pyridyl and hydrogen



Fig. 9 Packing diagram of dimer 2 showing the 2D sheet (dimer 4 has similar interactions).



substituents at C^2 only formed mononuclear tetrahedral copper(1) halide complexes.^{7b} The presence of bulky phenyl in place of hydrogen has altered the bonding behaviour of 2-benzoylpyridine thiosemicarbazone.

Acknowledgements

Financial support from Council of Scientific and Industrial Research, New Delhi (F.No.9/254(159)/2005-EMR-I), is grate-fully acknowledged. We are thankful to Prof. M. Zeller, Department of Chemistry, Youngstown State University, USA for partial help in X-ray studies. We thank Prof. R. N. Mukherjee, Department of Chemistry, IIT Kanpur for recording of ESR spectra.

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