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Thiosemicarbazone Derivatives of Copper(I): Influence of Substituents (*R*) at N^1 Atom of $[(C_5H_4N)HC^2{=}N^3N^2H\text{-}C^1(=S)N^1HR]$ in the Formation of 1D or 2D Networks of Copper(I) Complexes

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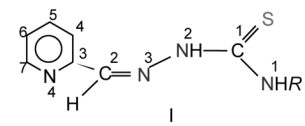
Abstract. Copper(I) halides with N^1-substituted pyridine-2-carbaldehyde thiosemicarbazones $[(C_5H_4N)HC^2{=}N^3N^2H\text{-}C^1(=S)N^1HR]$ in the presence of Ph_3P have formed complexes of stoichiometry, $[CuX(Hpytsc\text{-}N^1HR)(Ph_3P)_2]$ [*X*, *R*; Br, Me (**1**); Br, Et (**2**), Cl, Ph (**3**·CH_3CN)]. All these complexes are characterised by elemental analysis, IR and NMR (^1H, ^{31}P) spectroscopy and X-ray crystallography. The role of substituents at N^1 atom of pyridine-2-carbaldehyde thiosemicarbazones in intermolecular interactions in copper(I) complexes is described. A 1D polymer of compound **1** is formed by intermolecular $CH_{(methyl)}\cdots\pi_{(py)}$ interactions. The hydrogen atoms of EtN^1H and ethyl group interact with the phenyl ring of PPh_3 {via $EtN^1H\cdots\pi_{(Ph)}$, $H_2CH_{(Et)}\cdots\pi_{(Ph)}$} to form a 1D polymer of **2**. A 2D sheet arrangement of compound **3** is formed by pyridyl–phenyl ($CH_{(py)}\cdots\pi_{(Ph)}$) interactions along the *a* axis and phenyl–phenyl $[CH_{(Ph)}\cdots\pi_{(Ph)}]$ interactions (phenyl at N^1 with phenyl of PPh_3) along the *b* axis.

Introduction

Thiosemicarbazones, an important class of nitrogen, sulfur donors, received considerable attention due to their structural diversity [1, 2], variable-bonding modes [3], metallation properties [4], ion-sensing ability [5, 6], extraction properties [7] and pharmacological applications [8–10]. Thiosemicarbazones bearing a pyridine ring are known antitumor compounds and inhibitors of DNA synthesis and this activity is attributed to their ability to inhibit the DNA topoisomerase II enzyme responsible for the regulation of the topology of DNA [11, 12]. Since copper(II)-thiosemicarbazone compounds are used in biological systems, they may involve Cu^{II} reduction to Cu^{I} in the cells, thus the stability of Cu^{I} species is crucial to the hypotoxic reactivity and biological activity of topo-II inhibitors.

Pyridine-2-carbaldehyde thiosemicarbazone (I, Hpytsc-N^1H_2) with copper(I) halides in acetonitrile is known to form tetrahedral complexes, $[CuX(\eta^1\text{-}S\text{-}Hpytsc\text{-}N^1H_2)(Ph_3P)_2]$ [25]. In a recent study, the effect of substituents at the N^1 nitrogen atom on nature of bonding and nuclearity in copper(I) complexes with thiophene-2-carbaldehyde thiosemicarbazones was investigated. The substituents at the N^1 nitrogen atom changed the nature of bridging between two metal atoms and nuclearity of complexes [26]. In continuation, this paper reports the effect of substituents at the N^1 atom of pyridine-2-carbaldehyde thiosemicarbazone on the nuclearity and intermolecular interactions of complexes of copper(I) halides. These complexes were characterised using elemental analysis, IR and NMR (^1H, ^{31}P) spectroscopy and single crystal X-ray crystallography.



I

R

Me pyridine-2-carbaldehyde-N^1-methyl thiosemicarbazone (Hpytsc-N^1HMe)

Et pyridine-2-carbaldehyde-N^1-ethyl thiosemicarbazone (Hpytsc-N^1HEt)

Ph pyridine-2-carbaldehyde-N^1-phenyl thiosemicarbazone (Hpytsc-N^1HPh)

Experimental Section

Material and Techniques

Copper(I) bromide was prepared by the reduction of $CuSO_4\cdot5H_2O$ using SO_2 in the presence of NaBr in distilled water [27]. N^1-methyl thiosemicarbazide, N^1-ethyl thiosemicarbazide, pyridine-2-carbaldehyde and Ph_3P were procured from Aldrich Sigma Ltd. Pyridine-2-carbaldehyde-N^1-methyl-thiosemicarbazone and pyridine-2-carbaldehyde-N^1-ethyl-thiosemicarbazone ligands were prepared by condensation of pyridine-2-carbaldehyde with respective thiosemicarbazides. C, H and N analyses were carried out using a thermoelectron FLASH-EA1112 analyser. The melting points were determined with a Gallenkamp electrically heated apparatus. The IR spectra of the ligands and the complexes were recorded in the range, 4000–200 cm^{-1} (using KBr

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pellets) with a FTIR-SHIMADZU 8400 Fourier Transform Spectrophotometer and with a Pye–Unicam SP3–300 spectrophotometer. ^{1}H NMR spectra were recorded with a JEOL AL300 FT spectrometer at 300 MHz in $CDCl_3$ with TMS as the internal reference. ^{31}P NMR spectra were recorded at 121.5 MHz with *o*-phosphoric acid as the external reference taken as zero position.

Synthesis of Complexes

[CuBr(η^1-S-Hpytsc-N^{1}HMe)(Ph$_3$P)$_2$] (1): The ligand Hpytsc-N^{1}HMe (0.034 g, 0.174 mmol) was added to a solution of copper(I) bromide (0.025 g, 0.174 mmol) in acetonitrile (15 mL), and contents were stirred for 3–4 h. To the yellow precipitates thus formed Ph_3P (0.091 g, 0.358 mmol) was added followed by stirring for 5–10 min to form a yellow-coloured solution. On slow evaporation at room temperature it yielded yellow crystals. Yield, 0.109 g, 73 %, m. p. 200–202 °C. $C_{44}H_{40}BrCuN_4P_2S$ (862.28): calcd. C 61.29, H 4.64, N 6.50; found C 61.17, H 4.59, N 6.47. **IR** (KBr): $\tilde{\nu}$ =ν(N^{1}H), 3410s, ν(N^{2}H), 3200s, ν(C–H), 3096 w,3059w, 2965w, ν(C=N) + ν(C=C) 1640s, 1575s, ν(C–N), 1070s, 1029s, ν(C–S), 883s, ν(P–C$_{Ph}$) 1093(s). **^{1}H NMR** ($CDCl_3$): δ = 12.19 (–N^{2}H), 8.80s (C^{2}H), 8.69s (C^{7}H), 8.00s (C^{4}H), 7.83–7.31m (C^{5,6}H, Ph), 1.34d ($NHCH_3$). **^{31}P NMR** ($CDCl_3$): δ = –3.71, $\Delta\delta$ (δ complex – δ ligand) = 0.99.
Compounds **2** and **3** are prepared similarly.

[CuBr(η^1-S-Hpytsc-N^{1}HEt)(Ph$_3$P)$_2$] (2): Yield, 0.114 g, 75 %, m. p. 210–212 °C. $C_{45}H_{42}BrCuN_4P_2S$ (876.31): calcd. C 61.68, H 4.80, N 6.40; found C 61.74, H 4.59, N 6.33. **IR** (KBr): $\tilde{\nu}$ = (ν, N^{1}H) , 3420 (s, ν, N^{2}H) , 3265 (s, ν, C–H) 3075 (w), 2940 (w), 2910 (w), 2873 [w, ν, C=N) + ν(C=C] 1644 (s), 1570 (s, ν, C–N) , 1068 (s, ν, C–S) 884 (s, ν, P–C$_{Ph}$) 1095(s) cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ =12.74 (-N^{2}H), 8.74s (C^{2}H), 8.24s (C^{7}H), 7.99–7.30m (C^{4,6}H, PPh$_3$, N^{1}H), 7.12s (C^{5}H), 3.53m (–CH$_2$–), 1.36t (–CH$_3$). **^{31}P NMR** ($CDCl_3$): δ = –3.34, $\Delta\delta$ (δ complex – δ ligand) = 1.36.

[CuCl(η^1-S-Hpytsc-N^{1}HPh)(Ph$_3$P)$_2$]·CH$_3$CN (3·CH$_3$CN): Yield, 0.174 g, 75 %, m. p. 198–200 °C. $C_{51}H_{45}ClCuN_5P_2S$ (920.96): calcd. C 66.45, H 4.88, N 7.60; found C 66.72, H 4.79, N 7.56. **IR** (KBr): $\tilde{\nu}$ = (ν, N^{1}H) , 3432 (s, ν, N^{2}H) , 3260 (s, ν, C–H) 3180 (w), 3066 (w), 2910 (w), 2869 [w, ν, C=N) + ν(C=C] 1638 (s), 1574 (s, ν, C–N) , 1066 (s, ν, C–S) 885 (s, ν, P–C$_{Ph}$) 1095(s) cm^{-1}. **^{1}H NMR** ($CDCl_3$): 12.33s (-N^{2}H), 8.95s (C^{2}H), 8.54d (C^{7}H), 8.36s (NHPh), 7.54–7.31m (C^{4,5,6}H, PhN^{1}H, PPh$_3$). **^{31}P NMR** ($CDCl_3$): δ = –2.85, $\Delta\delta$ (δ complex – δ ligand) 1.85.

Hpytsc-N^{1}HPh: Pyridine-2-carbaldehyde (1.28 g, 11.9 mmol) was slowly added to a solution of *N*-phenylthiosemicarbazide (2.0 g, 11.9 mmol) in methanol (50 mL). The contents were heated under reflux for 6–7 h. The light yellow needles formed were dried and recrystallised from methanol. Slow evaporation of the solution gave clear light yellow crystals. 73 %, m. p. 205–207 °C. $C_{13}H_{12}N_4S$ (256.32): calcd. C 60.94, H 4.69, N 21.87; found C 60.56, H 4.59, N 21.72. **IR** (KBr): $\tilde{\nu}$ = (ν, N^{1}H) , 3415 (s, ν, N^{2}H) , 3250 (s, ν, C–H) 3195 (w), 3045 (w), 2915 (w), 2868 [w, ν, C=N) + ν(C=C] 1630 (s), 1585 (s, ν, C–N) , 1089 (s), 1051 (s, ν, C–S) 899s cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 11.34s (-N^{2}H), 8.85s (C^{2}H), 8.62d (C^{7}H), 8.47s (NHPh), 7.50–7.32m (C^{4,5,6}H, PhN^{1}H).

X-ray Crystallography

Crystals of **1**, **2** and **3**·CH_3CN were mounted on Bruker X8 KappaAPEXII, Enraf–Nonius CAD-4 and Oxford Diffraction Gemini R respectively, equipped with a graphite monochromator, and Mo-K_α radiation (λ = 0.71073 Å). Crystal data were collected at 100 K (**1**), 296 K (**2**) and 200 K (**3**·CH_3CN). The data were processed with APEX2 [28] and corrected for absorption using SADABS (transmissions factors: 1.000–0.856) [29] in **1**, processed with SMART and correct with SAINT in **2** and processed with CrysAlis CCD [30] and corrected with SCALE3 ABSPACK scaling algorithm in **3**·CH_3CN. The structure was solved by direct methods using the program SHELXS-97 [31] and refined by full-matrix least-squares techniques against F^2 using SHELXL-97 [32] in **1** and **3**·CH_3CN and XCAD-49 and SHELXTL in **2** [32]. Full details have been deposited with the Cambridge Crystallographic Data Centre, CCDC-773785 (**1**), -773786 (**2**) -773787 (**3**·CH_3CN), respectively. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk; or http:// www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): Syntheses of HpytscMe and HpytscEt, molecular structures of **2** and **3·CH$_3$CN**.

Results and Discussion

Synthesis and IR Spectroscopy

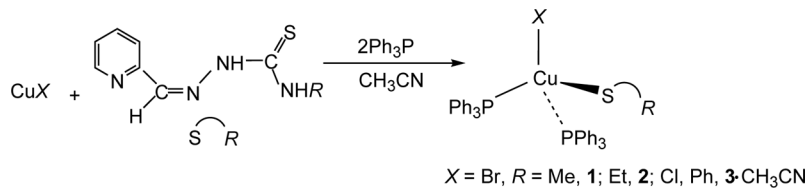
Scheme 1 represents the reaction of copper(I) halides (bromide or chloride) with pyridine-2-carbaldehyde N^1-substituted thiosemicarbazones. Copper(I) halides reacted with Hpytsc-N^{1}HMe, Hpytsc-N^{1}HEt or Hpytsc-N^{1}Ph in 1:1 molar ratio and formed insoluble precipitates. The addition of two mmols of Ph_3P to these precipitates in situ formed clear solutions, which on slow evaporation yielded compounds of empirical formula, [Cu*X*(η^1-S-Hpytsc-N^{1}H*R*)(Ph$_3$P)$_2$] [*X*, *R*; Br, Me (**1**); Br, Et (**2**); Cl, Ph (**3**·CH_3CN)]. If copper(I) halides were treated with Ph_3P first, the addition of thio-ligands did not form clear solution and no crystalline product could be obtained and thus first route was adopted.

The coordination of the neutral ligands in the complexes **1**–**3**·CH_3CN is supported by the presence of ν(N–H) bands in the ranges 3410–3420 cm^{-1} (due to –N^{1}HR) and 3200–3265 cm^{-1} (due to–N^{2}H–). The most characteristic thioamide bands due to ν(C=S) lie in the range 883–885 cm^{-1} in complexes and undergo low energy shifts (free ligands, 895–899 cm^{-1}). The ν(C–H) and ν(P–C$_{Ph}$) bands appeared in the ranges, 2869–2975 cm^{-1} and 1093–1095 cm^{-1} respectively.

Crystal Structures of Complexes 1–3·CH$_3$CN

The complexes **1**–**3**·CH_3CN crystallised in monoclinic system with space group *P*2(1)/*c*. The crystallograhic data and important bond parameters are given in Table 1 and 2 respectively. The molecular structure of representative complex **1** is given in Figure 1

One thio-ligand, one bromine atom and two Ph_3P ligands are coordinated to copper(I) atom in complexes **1** and **2**. The Cu–Br bond lengths, {2.5217(3) **1**; 2.5302(3) Å **2**} are similar to the analogous complex, [CuBr(Hpytsc-N^{1}H$_2$)(Ph$_3$P)$_2$] (**4**) (2.5475(8) Å) [25]. These distances are less than the sum of



Scheme 1.

Table 1. Crystallographic data of complexes **1**–**3**.

	1	**2**	**3**·CH_3CN
Empirical formula	$C_{44}H_{40}BrCuN_4P_2S$	$C_{45}H_{42}BrCuN_4P_2S$	$C_{51}H_{45}ClCuN_5P_2S$
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P 21/c (No. 14)	$P2_1/c$	$P121/c1$
a /Å	10.10030(10)	9.9659(5)	18.8154(14)
b /Å	17.1516(2)	17.5745(8)	11.2125(10)
c /Å	22.7050(3)	22.9750(11)	21.6783(15)
α /°	90	90	90
β /°	94.4200(10)	95.3760(10)	96.450(7)
γ /°	90	90	90
V /Å^3	3921.63(8)	4006.3(3)	4544.5(6)
Z	4	4	4
$D_{calcd.}$ /g·cm^{-3}	1.460	1.453	1.346
μ (Mo) /mm^{-1}	1.748	1.713	0.697
λ (Mo-K_α) /Å	0.71073	0.71073	0.71073
F(000)	1768	1800	1912
T /K	100(2)	100(2)	200(2)
Reflections collected	94055	9925	8095
Reflections observed, [$I > 2\sigma(I)$]	6813	8566	3057
Parameters	478	488	551
R (all data)	0.0381	0.0389	0.2080
R_w (all data)	0.0605	0.0855	0.0936
Goodness-of-fit on F^2	1.049	1.049	0.898

Table 2. Bond lengths /Å and bond angles /° of complexes **1**–**3**.

[CuBr(η^1-S-Hpytsc-N^{1}HMe)(Ph_3P)$_2$] (**1**)			
Cu(1)–Br(1)	2.5217(3)	S(1)–C(17)	1.693(2)
Cu(1)–P(1)	2.2700(5)	C(17)–N(14)	1.325(3)
Cu(1)–P(2)	2.2860(5)	N(13)–C(17)	1.340(3)
Cu(1)–S(1)	2.4123(6)	N(13)–N(12)	1.370(12)
Br(1)–Cu(1)–P(1)	104.004(16)	P(2)–Cu(1)–S(1)	94.373(19)
Br(1)–Cu(1)–P(2)	109.513(15)	S(1)–Cu(1)–P(1)	109.273(19)
P(1)–Cu(1)–P(2)	126.28(2)	S(1)–Cu(1)–Br(1)	113.221(15)
[CuBr(η^1-S-Hpytsc-N^{1}HEt)(Ph_3P)$_2$] (**2**)			
Cu(1)–Br(1)	2.5302(3)	S(1)–C(39)	1.6957(19)
Cu(1)–P(1)	2.2996(5)	C(39)–N(1)	1.326(2)
Cu(1)–P(2)	2.2842(5)	N(2)–C(39)	1.353(2)
Cu(1)–S(1)	2.4081(5)	N(2)–N(3)	1.366(2)
Br(1)–Cu(1)–P(1)	108.860(15)	P(2)–Cu(1)–S(1)	107.363(17)
Br(1)–Cu(1)–P(2)	105.418(14)	S(1)–Cu(1)–P(1)	94.721(17)
P(1)–Cu(1)–P(2)	127.095(18)	S(1)–Cu(1)–Br(1)	113.133(14)
[CuCl(η^1-S-Hpytsc-N^{1}HPh)(Ph_3P)$_2$] (**3**)			
Cu–P(1)	2.2669(14)	S–C(1)	1.680(6)
Cu–P(2)	2.3016(18)	N(1)–C1	1.349(6)
Cu–Cl	2.3892(17)	N(1)–N(2)	1.380(5)
Cu–S	2.4041(15)	N(2)–C(2)	1.276(6)
P(1)–Cu–P(2)	123.09(7)	P(1)–Cu–S	112.61(6)
P(1)–Cu–Cl	103.60(6)	P(2)–Cu–S	100.32(6)
P(2)–Cu–Cl	107.98(6)	Cl–Cu–S	108.77(6)

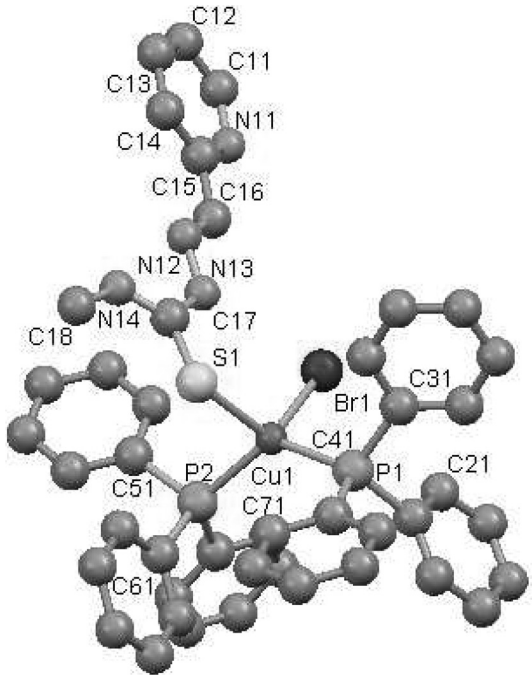
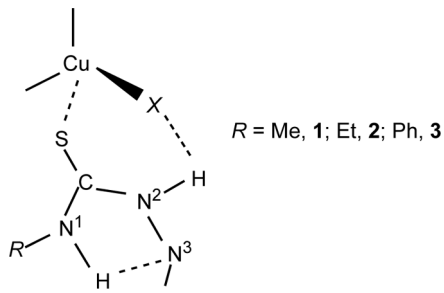


Figure 1. Molecular structure of [CuBr(η^1-S-Hpytsc-N^{1}HMe)(Ph_3P)$_2$] **(1)** (structures of **2** and **3** are similar).

ionic radii of Cu^+ and Br^- (2.73 Å) [33]. Similar coordination is found in complex **3**·CH_3CN. In this complex, the Cu–Cl distance of 2.3892(17) Å is shorter than 2.4097(6) Å in [CuCl(Hpytsc-N^{1}H$_2$)(Ph_3P)$_2$]·CH_3CN (**5**). The Cu–P distances in **1**–**3**·CH_3CN are close to the literature values [25]. Table 3 shows a comparison of some important bond parameters of copper(I) halide complexes with pyridine-2-carbaldehyde thiosemicarbazones. Keeping the halogen constant, Cu–S and C–S bond show a gradual change with the change of substituent at N^1 atom. The bond angles around the copper atom revealed distorted tetrahedral arrangement. The P–Cu–P bond angles are affected by substitution, largest being with Hpytsc-N^{1}HEt (**2**) ligand and smallest being with Hpytsc-N^{1}H$_2$ (**4** [25]). The Cu–S–C bite angles are large in complexes **1**–**3**·CH_3CN relative to literature reports [25].

Packing Networks

In complexes **1**–**3**·CH_3CN, imino hydrogen atoms form intramolecular hydrogen bonding with the halogen atoms, (–N^{2}H···*X*), which is similar to that in **4** and **5** [25]. However, the intermolecular hydrogen bonding is different in all the three complexes and is influenced by the substituents at N^1 atom of the thio-ligand.



In complex **1**, methyl substituent at the N^1 atom interacts intermolecularly with pyridyl ring at the C^2 atom of the second molecule through $CH_{(methyl)}\cdots\pi_{(py)}$ (2.888, 2.867 Å), which generates a linear 1D polymer (Figure 2).

In complex **2**, replacement of methyl group with the ethyl group at N^1 changed the intermolecular interactions. In complex **2**, the phenyl rings of Ph_3P molecule are bonded intermolecularly to EtN^{1}H, CH_3 of ethyl group and phenyl ring of second Ph_3P molecule through EtN^{1}H···$\pi_{(Ph)}$ (2.858 Å), $CH_{(Et)}\cdots\pi_{(Ph)}$ (2.805 Å) and $CH_{(Ph)}\cdots\pi_{(Ph)}$ (2.862 Å). These interactions result in the formation of a linear polymer (Figure 3). Interestingly, in the earlier reported complex [CuBr(Hpytsc-N^{1}H$_2$)(Ph_3P)$_2$] (**4**) [25], no intermolecular interactions were observed.

Intermolecular interactions are different in complex **3**·CH_3CN. Both the pyridyl ring at the C^2 carbon atom and phenyl ring at the N^1 nitrogen atom take part in the intermolecular interactions. A linear chain is formed by the interaction of the pyridyl ring with the phenyl ring of PPh_3 by $CH_{(py)}\cdots\pi_{(Ph)}$ (2.875 Å). The two linear chains are further connected by the following interactions: phenyl ring at N^1 atom with phenyl ring of PPh_3 ($CH_{(Ph)}\cdots\pi_{(Ph)}$, 2.830 Å) and amino hydrogen with phenyl ring of PPh_3 (PhN^{1}H···$\pi_{(Ph)}$, 2.864 Å). This results in the formation of a sheet structure (Figure 4). In contrast, [CuCl(η^1-S-Hpytsc-N^{1}H$_2$)(Ph_3P)$_2$]·CH_3CN (**5**) formed a hydrogen bonded trimer [25]. The acetonitrile molecules are forming $H_2CH\cdots Cl$ bonds (2.886 Å) and are lying between the chains.

Solution-Phase Behaviour

The N^{2}H NMR spectroscopic signal of the ligands appear at 12.19 ppm, 12.74 ppm and 12.33 ppm in the complexes **1**, **2** and **3** respectively, which are at low field relative to uncoordinated ligands (Hpytsc-N^{1}HMe, 11.26; Hpytsc-N^{1}HEt, 11.21; Hpytsc-N^{1}HPh, 11.34 ppm). This indicates coordination of

Table 3. Comparison of important bond parameters /Å, ° of copper(I) halide complexes.

Complex	Cu–S	C–S	Cu–P	Cu–S–C	P–Cu–P
[CuBr(Hpytsc-N^{1}H$_2$)(Ph_3P)$_2$] (**4**)[25]	2.4142(3)	1.690(5)	2.2785(19) 2.2995(13)	105.82(15)	122.39(5)
[CuBr(Hpytsc-N^{1}HMe)(Ph_3P)$_2$] (**1**)	2.4123(6)	1.693(2)	2.2700(5), 2.2860(5)	110.81(7)	126.28(2)
[CuBr(Hpytsc-N^{1}HEt)(Ph_3P)$_2$] (**2**)	2.4081(5)	1.6957(19)	2.2996(5), 2.2842(5)	111.79(6)	127.095(18)
[CuCl(Hpytsc-N^{1}H$_2$)(Ph_3P)$_2$] (**5**)[25]	2.4063(6)	1.706(2)	2.2622(6), 2.2911(6)	103.13(8)	121.53(2)
[CuCl(Hpytsc-N^{1}HPh)(Ph_3P)$_2$] (**3**)·CH_3CN	2.4041(15)	1.680(6)	2.2669(14), 2.3016(18)	110.2(2),	123.09(9)

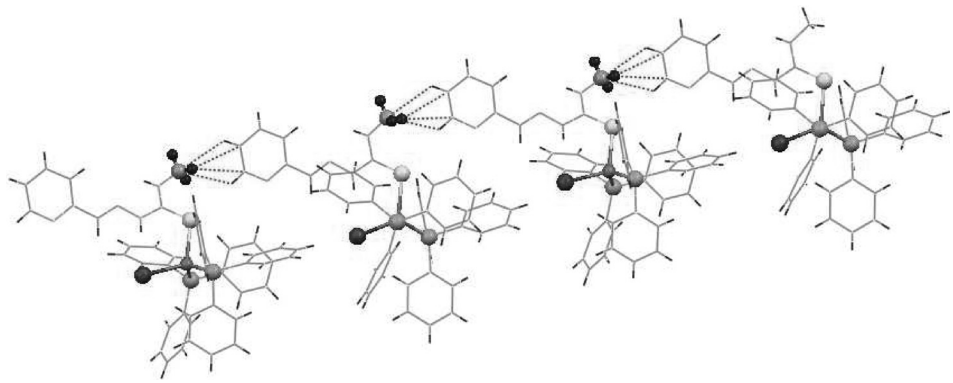


Figure 2. Packing diagram of [CuBr(η^1-S-Hpytsc-N^1HMe)(Ph_3P)$_2$] (**1**).

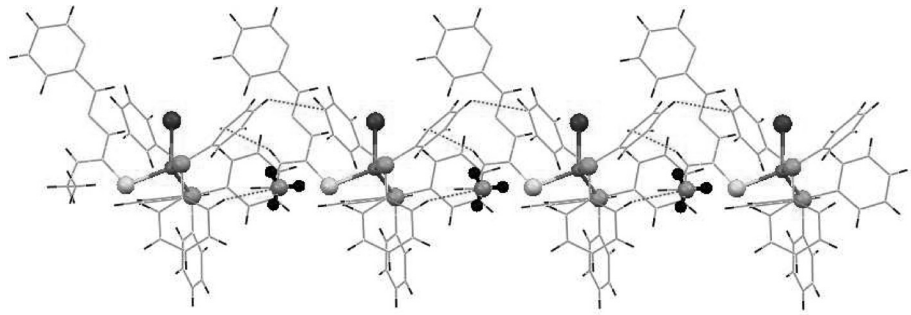


Figure 3. Packing diagram of [CuBr(η^1-S-Hpytsc-N^1HEt)(Ph_3P)$_2$] (**2**).

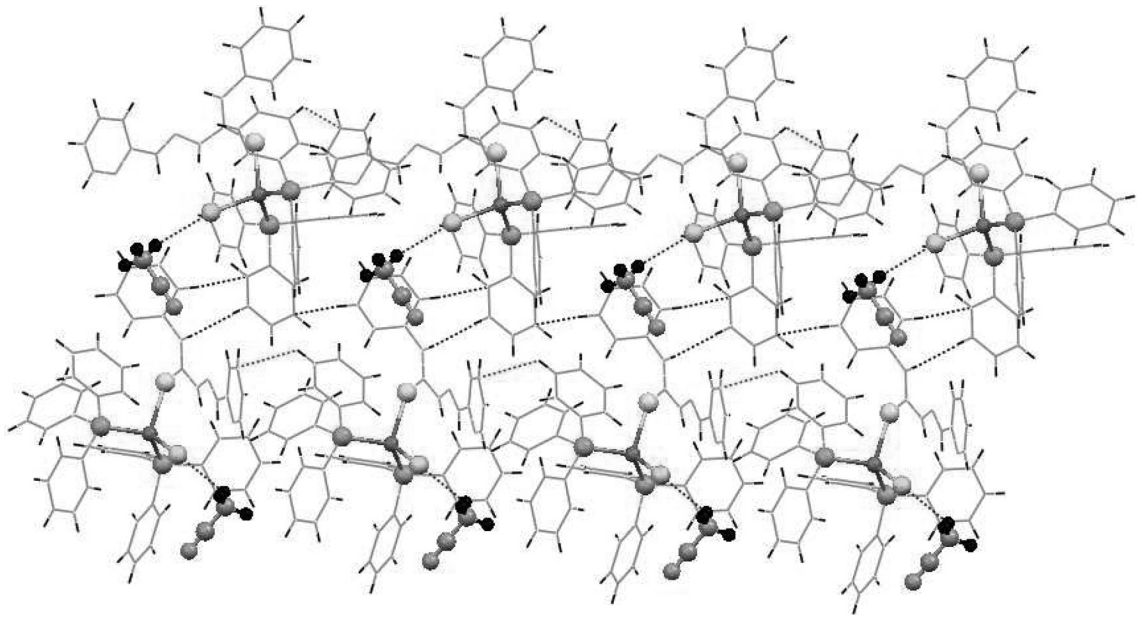


Figure 4. Packing diagram of [CuCl(η^1-S-Hpytsc-N^1HPh)(Ph_3P)$_2$]·CH_3CN (**3**·CH_3CN).

neutral ligands to copper(I) metal atom. Furthermore, the C^2H signals at 8.80 ppm(**1**); 8.74 ppm(**2**) and 8.95 ppm (**3**·CH_3CN) also showed lowfield shifts. The methyl protons of $-N^1HCH_3$ appeared as a doublet signal at 1.34 ppm in **1**. The ethyl protons of $-N^1HC_2H_5$ group appeared as two sets, one multiplet (3.53 ppm, CH_2); and one triplet signal (1.36 ppm, CH_3) in complex **2**. The C^4H and C^6H at pyridyl ring protons in complex **1** and C^4H, C^5H and C^6H of pyridyl ring protons in **2** and **3**·CH_3CN merged with ring protons of Ph_3P (7.31–7.83 ppm). The ^{31}P NMR spectrum of each complex showed one signal

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at –3.71 ppm (**1**), –3.34 ppm (**2**) and –2.85 ppm (**3**·CH_3CN) with coordination shifts of 0.99, 1.36 and 1.85 ppm respectively. This trend is similar to those observed in case of tetrahedral monomers in literature [3, 25] and indicates that the structure of complexes remains intact in the solution phase.

Conclusions

It is concluded here that there is no effect of substitution at N^1 on the nuclearity of complexes. However, the presence of the groups at the N^1 atom changed intermolecular interactions, which resulted in the formation of 1D and 2D networks. The latter behaviour is in contrast to the unsubstituted (at N^1) pyridine-2-carbaldehyde thiosemicarbazone. The molecular structure remains unchanged in the solution state as revealed by ^1H and ^{31}P NMR spectroscopy.

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References

[1] J. S. Casas, M. S. Garcia-Tasende, J. Sordo, *Coord. Chem. Rev.* **2000**, *209*, 197.
[2] D. R. Smith, *Coord. Chem. Rev.* **1997**, *164*, 575.
[3] T. S. Lobana, Rekha, A. P. S. Pannu, G. Hundal, R. J. Butcher, A. Castineiras, *Polyhedron* **2007**, *26*, 2621and references cited therein.
[4] T. S. Lobana, G. Bawa, G. Hundal, M. Zeller, *Z. Anorg. Allg. Chem.* **2008**, *634*, 931.
[5] R. K. Mahajan, I. Kaur, T. S. Lobana, *Talanta* **2003**, *59*, 101.
[6] R. K. Mahajan, I. Kaur, T. S. Lobana, *Ind. J. Chem.* **2006**, *45A*, 639.
[7] K. J. Reddy, J. R. Kumar, C. Ramachandraiah, T. Thriveni, A. V. Reddy, *Food Chem.* **2007**, *101*, 585.
[8] M. A. Ali, M. E. Khalifa, S. E. Ghazy, M. M. Hassanien, *Anal. Sci.* **2002**, *18*, 1235.
[9] M. B. Ferrari, F. Bisceglie, G. Pelosi, P. Tarasconi, R. Albertini, A. Bonati, P. Lunghi, S. Pinelli, *J. Inorg. Biochem.* **2001**, *83*, 169.
[10] K. Nomiya, K. Sekino, M. Ishiawa, A. Honda, M. Yokoyama, N. C. Kasuga, H. Yokoyama, S. Nakano, K. Onodera, *J. Inorg. Biochem.* **2004**, *98*, 601.
[11] J. Easmon, G. Purstinger, G. Heinisch, T. Roth, H. H. Fiebig, W. Holzer, W. Jager, M. Jenny, J. Hofmann, *J. Med. Chem.* **2001**, *44*, 2164.
[12] J. S. Lewis, J. Easmon, J. R. Rutlin, L. A. Jones, M. J. Welch, *J. Labelled Compd. Radiopharm.* **2003**, *46*, S388.
[13] A. Sreekanth, M. R. P. Kurup, *Polyhedron* **2003**, *22*, 3321.
[14] D. X. West, I. S. Billeh, G. A. Bain, J. Valdes-Martinez, K. H. Ebert, S. Hernandez-Ortega, *Trans.-Met. Chem.* **1996**, *21*, 573.
[15] D. X. West, J. S. Ives, J. Krejci, M. M. Salberg, T. L. Zumbahlen, G. A. Bain, A. E. Liberta, J. Valdes-Martinez, S. Hernadez-Ortiz, R. A. Toscano, *Polyhedron* **1995**, *14*, 2189.
[16] V. A. Neverov, V. N. Byushkin, *Coord. Chem.* **1983**, *9*, 1695.
[17] E. W. Ainscough, A. M. Brodie, J. D. Ranford, J. M. Waters, *J. Chem. Soc., Dalton Trans.* **1991**, 2125.
[18] D. X. West, Y. Yang, T. L. Klein, K. I. Goldberg, A. E. Liberta, J. Valdes-Martinez, R. A. Toscano, *Polyhedron* **1995**, *14*, 1681.
[19] P. Souza, A. I. Matesanz, F. Fernandez, *J. Chem. Soc., Dalton Trans.* **1996**, 3011.
[20] P. Gomez-Saiz, J. Garcia-Tojal, M. Maestro, J. Mahia, L. Lezama, T. Rojo, *Eur. J. Inorg. Chem.* **2003**, 2123.
[21] E. W. Ainscough, A. M. Brodie, J. D. Ranford, J. M. Waters, *J. Chem. Soc., Dalton Trans.* **1991**, 2125.
[22] P. Gomez-Saiz, J. Garcia-Tojal, M. A. Maestro, J. Mahia, F. J. Arniaz, L. Lezama, T. Rojo, *Eur. J. Inorg. Chem.* **2003**, 2639.
[23] J. Garcia-Tojal, L. Lezama, J. L. Pizarro, M. Insausti, M. I. Arriortua, T. Rojo, *Polyhedron* **1999**, *18*, 3703.
[24] E. Bermejo, A. Castineiras, M. Gil, E. Labisbal, A. Sousa, H. Beraldo, D. X. West, *Z. Anorg. Allg. Chem.* **2001**, *627*, 827.
[25] T. S. Lobana, Rekha, R. J. Butcher, A. Castineiras, E. Bermejo, P. V. Bharatam, *Inorg. Chem.* **1535**, *45*, 1535.
[26] T. S. Lobana, R. Sharma, A. Castineiras, G. Hundal, R. J. Butcher, *Inorg. Chim. Acta* **2009**, *362*, 3547.
[27] G. Brauer, *Handbook of Preparative Chemistry*, 2nd ed., Academic Press, New York, **1965**, vol. 2.
[28] Bruker, *APEX2* Software, Bruker AXS Inc. V2.0–1, Madison, Wisconsin, USA. **2005**.
[29] G. M. Sheldrick, *SADABS*, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany **1997**.
[30] Bruker. *SMART* and *SAINT*, Area Detector Control and Integration Software, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin,USA, **1997**.
[31] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
[32] G. M. Sheldrick, *SHELXL-97*. Program for the Refinement of Crystal Structures. University of Goettingen, Germany, **1997**.
[33] J. E. Huheey,E. A. Keiter,R. L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed., Harper Collins College, Publishers, New York, **1993**.

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