Synthesis And Characterization Of 4-Cyanobenzaldeyde And 4 Methyl Benzaldehyde With Cu(I) Halides

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Abstract:Copper (I) halides (X = Cl, Br, I) were reacted with one mole of 4-cyanobenzaldehyde thiosemicarbazone (HL^1) and two molar Ph_3P to form complexes of general formula, $[CuX(HL^1)(Ph_3P)_2]$ (1-3). However, the similar reaction with 4-methylbenzaldehyde thiosemicarbazone (HL^2) did not give the same complex with copper (I) iodide and bromide. Instead of that X = I (A), Br (B) complexes of stiochiometry, $[CuX(Ph_3P)_3]$ formed. No ligand gets attached to copper centre. Only the copper (I) chloride has formed complex of stiochiometry, $[CuCl(HL^2)(Ph_3P)_2]$ 4. Conformation of formation of complexes was done by infra-red, ultra-violet and nuclear magnetic resonance spectroscopy. All these techniques support binding of thio- ligand to copper center in neutral mode. Binding of trihenylphosphine in these complexes is also confirmed by these techniques.

Keywords: Thiosemicarbazone, NMR spectroscopy, monomer, tetrahedral, ligand, copper(I) halides

Introduction:

Thiosemicarbazones are important N, S- donors ligands. The importance of thiosemicarbazone lies in their structural diversity, variable bonding modes, ions sensing ability, metal extraction properties and biological activities [1-16]. A number of complexes of thiosemicarbazones with copper(I) halides have been reported. These complexes can be broadly divided into three categories: i) Monomers: a) four coordinated tetrahedral monomers having general formula, $[CuX(Htsc)(Ph_3P)_2]$ (A) [2-4,17-24]; b) three coordinated planer monomers of formula, $[CuX(Htsc)_2]$ (B) and $[CuX(Htsc)(Ph_3P)]$ (C) [23, 24], ii) Dimers: a) halogen-bridged dimers, $[Cu_2(\mu\text{-}X)_2(Htsc)_2(Ph_3P)_2]$(D) [2-4,19-24]; b) sulfur-bridged dimers of formula, $[Cu_2(\mu\text{-}S\text{-}Htsc)_2X_2(Ph_3P)_2]$ (E) [23] and $[Cu_2(\mu\text{-}S\text{-}Htsc)_2X_2(Htsc)_2]$ (F) [2-4,19-21], and iii) Miscellaneous complexes (G) [3] (Chart 1).

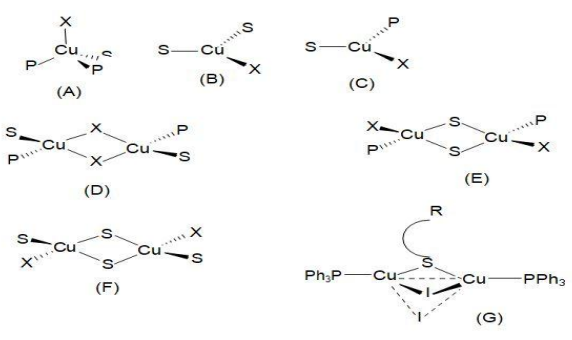


Chart 1

In present paper, synthesis of complexes of copper(I) halides with 4-cyanobenzaldehyde thiosemicarbazone (4-CNHbtsc, HL^1) and 4-methylbenzaldehyde thiosemicarbazone (4-MeHbtsc, HL^2) is given. Synthesized ligands and complexes were characterized using IR, UV and ^1H NMR spectroscopic techniques.

Experimental

Material

Purchasing of 4-cyanobenzaldehyde, 4-methylbenzaldehyde, PPh_3 and thiosemicarbazide was done from Calibochem Ltd. The melting point, Infra-red (IR) spectra, Ultra-violet (UV) spectra and ^1H NMR spectra were recorded using lab fit electrically heated, SHIMADZU FTIR 8400S, SHIMADZU UV-1800 spectrophotometer and BRUCKER ADVANCE I.I 400 NMR Spectrometer respectively.

Synthesis:

4-cyanobenzaldehyde and 4-methylbenzaldehyde were refluxed with thiosemicarbazide in 1 : 1 molar ratio in methonal for 5-6 hours to form 4-cyanobenzaldehyde thiosemicarbazone (4-CNHbtsc, HL^1) and 4-methylbenzaldehyde thiosemicarbazone (4-MeHbtsc, HL^2) respectively.

4-cyanobenzaldehyde thiosemicarbazone (4-CNHbtsc, H^1L). M.P. 160-162°C, Yield 0.0203g, 60 %. UV transition (methanol, nm): $n\rightarrow\pi^*$, 331; $\pi\rightarrow\pi^*$, 228. IR spectrum in cm^{-1}: stretching N-H, 3417, 3248; -NH-, 3152; C=C, C=N, 1535, 1500, 1600; C-H, 2978; C=S, 831. ^1H NMR (DMSO, δppm): 11.59 (s, N^2H, 1H), 8.01 (s, C^2H), 8.13, 7.88 (s, NH_2) 7.86 (d, $C^{5,6}H$), 7.65 (d, $C^{4,8}H$).

4-methylbenzaldehyde thiosemicarbazone (4-MeHbtsc, H^2L). M.P.120-122°C. Yield 0.196 g, 62%.UV transition (methanol, nm): $n\rightarrow\pi^*$, 305; $\pi\rightarrow\pi^*$, 239. IR spectrum in cm^{-1}: stretching N-H, 3372, 3262; -NH-, 3179; C=C, C=N, 1620, 1532, 1645; C=S, 800. ^1H NMR (DMSO, δ ppm): 11.39 (s, N^2H, 1H), 8.04 (s, C^2H, 1H), 7.66 (O-$C^{4,8}H$), 8.17, 7.94 (s, NH_2).

$[CuI(HL^1)(PPh3)2]$ 1: To a stirred solution of CuI (0.025g, 0.013mmol) in 20 ml acetonitrile was added solid ligand HL^1 (0.026 g ,0.0127mmol) and stirred for 4 hours and Pale yellow solid form and was added PPh_3 (0.068 g, 0.029mmol).The solution was further stirred for 5 min. and filtered. M.P. 220-221^{o}C. Highly soluble in acetonitrile, partially in chloroform. Yield 0.059 g, 70%. UV transition (acetonitrile, nm): 343; 235, 260. IR spectrum in cm^{-1}: stretching N-H, 3458, 3345; -NH-, 3070; C-H, 2879; C=C, C=N, 1528, 1501,1587; C=S, 824; C-P_{Ph},1094 .^1H NMR (CDCl3, □□ppm): 11.88 (s, N^2H); 8.23 (s, C^2H); 6.85, 6.05 (s, NH_2), 7.73-7.71(m, Ph); 7.46-7.26 (m-, o-, p-, PPh_3).

Complexes **2-4** were synthesized using same procedure.

$[CuBr(HL^1)(PPh_3)_2]$ 2. M.P.170-172^{o}C**.** Highly soluble inacetonitrile, partially soluble in chloroform. Yield, 0.063 g, 65%. UV transition (acetonitrile, nm): 328, 233, 255. IR spectrum in cm^{-1}: Stretching N-H, 3448, 3289;-NH-, 3167; C-H, 2935; C=C, C=N, 1339, 1475, 1595; C=S, 825; C-P_{Ph}), 1092. ^1H NMR ($CDCl_3$,δ ppm):12.53 (s, N^2H); 8.17(s, C^2H); 6.85, 6.01 (s, NH_2); 7.71-7.65 (m, Ph); 7.44-7.19 (m-, o-, p-, PPh_3).

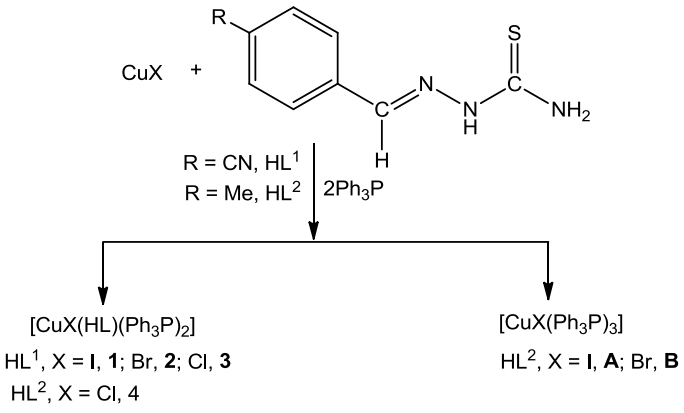
$[CuCl(HL^1)(PPh3)2]$ 3. M.P. 135 – 136^o C, highly soluble in acetonitrile, partially soluble in chloroform. Yield 0.093 g, 67%. UV transition (acetonitrile, nm): 334; 218, 254. IR spectrum in cm^{-1}: Stretching N-H, 3447, 3287; -NH-, 3049; C-H, 2879; C=C + C=N, 1547, 1475, 1593; C=S, 824; C-P_{Ph}, 1092. ^1H NMR (CDCl3, □ppm): 13.04 (s, N^2H);

8.01(s, C^2H); 6.76, 6.00 (s, NH_2); 7.63 (d, $C^{5,7}H$); 7.53 (d,$C^{4,8}H$); 7.42-7.12 (PPh_3).

[$CuCl(HL^2)(PPh_3)_2$] 6. M.P. 120-122°C. Highly soluble in acetonitrile, partially soluble in chloroform. Yield 0.083g, 64% UV transistion (acetonitrile, nm): 313; 233, 262. IR spectrum in cm^{-1}: Stretching N-H, 3463, 3321; -NH-, 3121; C=C, C=N, 1551, 1479, 1589; C-H, 2951; C=S, 813; P-C_{Ph}, 1092. ^1H NMR ($CDCl_3$, δ ppm): 12.61 (s, N^2H); 8.13 (s, C^2H); 6.91, 6.09 (s, NH_2); 7.55-7.45 (m, Ph); 7.44-7.20 (m-, o-, p-, PPh_3).

Results and Discussion

Copper (I) halides (X = Cl, Br, I) were reacted with one mole of 4-cyanobenzaldehyde thiosemicarbazone (HL^1) and two molar Ph_3P to form complexes of general formula, [$CuX(HL^1)(Ph_3P)_2$] (Scheme 1)**.** However, same reaction with 4-methylbenzaldehyde thiosemicarbazone (HL^2) did not give the same complex with copper (I) iodide and bromide. Instead of that X = I (**A**), Br (**B**) complexes of stiochiometry, [$CuX(Ph_3P)_3$] formed. No ligand gets attached to copper centre. Only the copper (I) chloride has formed complex of stiochiometry, [$CuCl(HL^2)(Ph_3P)_2$] **4**. The whole reaction sequence has been summarized in scheme 1.



Scheme 1

Discussion on UV Spectroscopy

Since nitrogen and sulfur atom are present in ligands and attached to the carbon via double bond, n→π* transition in HL^1 and HL^2 appeared at 331 nm and 305 nm respectively. This band showed shift to lower wavelength 343 (**1**), 334 (**3**), 313 **(4)** nm in complexes **1**, **3** and **4** as compare to free ligand, indicating coordination of ligand to metal centre. Electronic transition from Pi bonding orbital to pi anti-bonding orbital also showed same trands. Additional peaks at 260 nm (**1**), 255 nm (**2**), 254 nm (**3**), 262 nm (**4**) due to phenyl ring of triphenyl phosphine has been observed and confirmed its coordination to copper(I).

Discussion on IR:

The □(N-H) peaks of thiosemicarbazone ligands can be divided into two categories:(i) Asymmetric stretching appeared in the range, 3321-3463cm^{-1}. (ii) Symmetric stretching appeared in the range 3248-3289 cm^{-1}. Amide stretching appeared in the range, 3049-3167

cm^{-1} in ligands (Table 1). Presence of all these three bands in complexes ensured binding of thio- ligand in neutral form and coordination through thione sulfur. The characteristic band of thiosemicarbazone □(C=S), appeared at 831 cm^{-1} and 800 cm^{-1} in HL^1, HL^2 respectively. Low energy shift at 824 cm^{-1} (**1**), 825 cm^{-1} (**2**) and 824 cm^{-1} (**3**) of this band is attributed to the weakening of C=S band due to the binding of sulfur atom to metal centre. Additional stretching □(P-CPh) band in the range 1094-1092 cm^{-1} in complexes (**1-3**, **4**) supported the binding of Ph3P to the copper centre.

Table 1. Important IR peaks

Name	ν(N-H)	ν(-NH-)	ν(C=C)+ ν(C=N)+ δ(NH_2)	ν(C-H)	ν(C=S)	ν(P-C_{Ph})
Ph_3P	-	-	-	3059		1087
HL^1	3417,3248	3152	1535,1500,1600	2978	831	-
[CuI(HL^1)(Ph_3P)$_2$]**1**	3458,3345	3070	1528,1501,1587	2947	824	1094
[CuBr(HL^1)(Ph_3P)] **2**	3448,3289	3167	1339,1475,1595	2935	825	1092
[CuCl(HL^1)(Ph_3P)] **3**	3447,3287	3049	1547,1475,1593	2879	824	1092
HL^2	3372,3262	3179	1620,1532,1645	-	800	-
[CuCl(HL^2)(Ph_3P)] **4**	3463,3321	3121	1551,1479,1589	2951	813	1092

Discussion on NMR

In HL^1 and HL^2 the ^1H NMR signal due to N^2H – proton appeared at δ 11.59 ppm and δ 11.39 ppm respectively. In complexes, **1-3,** this proton showed down field shift as compare to ligands. The shift in N^2H proton is in order **3** > **2** > **1**.

The electronegative halogen atom withdraw the electron density from N^2H through H-bonding and cause de-shielding which resulted into down field shift. The electronegativity increases as Cl > Br > I thus the shift also increased in same way. The same pattern is observed in complex **4**, NH_2 gave two singlets at δ 8.13 ppm and δ 7.88 ppm in free ligands indicating their magnetically non–equivalent behaviour of two protons. On complexation to copper (I) centre, these proton showed siginificant up field shift δ 6.85-6.00 ppm (**1-3**) vis –a vis free ligand. In free ligands, lone pair of electron on nitrogen of NH_2 group in resonance with (C=S), thus delocalization of lone pair of electron causes deshielding where as, on bonding this delocalization stops and lone pair became localized, which causes shielding and resulted into high field shift in complexes (**1-3, 4**).

The presence of these protons (N^2H, NH_2) ensured the coordination of thiosemicarbazones as neutral ligands. Ring protons of ligands appeared in range δ 7.86-7.45

ppm in ligands and their complexes (**1-3**, **4**).The additional ring protons due to PPh3 molecule appeared in range δ 7.46-7.12 ppm in complexes (**1-3**, **4**) indicate bonding of PPh3 to metal centre.C^2H proton in free ligands appeared at δ 8.01 ppm(HL^1) and δ 8.04 ppm (HL^2). This proton showed no significant shift and appeared in range δ 8.01-8.03 ppm in complexes (**1-3, 4**). The additional ring protons due to PPh3 molecule appeared in range 7.46-7.12 ppm in complexes (**1-3**, **4**) indicate bonding of PPh3 to metal centre. The C^2H proton in free ligands appeared at 8.01 ppm (HL^1) and 8.04 ppm (HL^2).This proton showed no significant shift and appeared in range 8.01-8.03 ppm in complexes (**1-3, 4**).

Table 2. ^1H NMR signals of HL^1, HL^2 and **1-4**

Name	N^2H	C^2H	NH_2	Ring proton Of ligand	Ph_3P ring proton
HL^1	11.59(s)	8.01(s)	8.13(s) 7.88(s)	7.86(d,$C^{5,7}H$) 7.65(d,$C^{4,8}H$)	-
[CuI(HL^1)(Ph_3P)$_2$] **1**	11.88(s)	8.23(s)	6.85(s) 6.05(s)	7.73-7.71(m)	7.76-7.26(m)
[CuBr(HL^1)(Ph_3P)] **2**	12.53(s)	8.17(s)	6.85(s) 6.01(s)	7.71-7.65(m)	7.44-7.16(m)
[CuCl(HL^1)(Ph_3P)] **3**	13.04(s)	8.01(s)	6.76(s) 6.00(s)	7.63(d,$C^{5,7}H$) 7.53(d,$C^{4,8}H$)	7.42-7.12(m)
HL^2	11.39(s)	8.04(s)	8.17(s) 7.94(s)	7.66(d,$C^{4,8}H$)	-
[CuCl(HL^2)(Ph_3P)] **4**	12.61(s)	8.13(s)	6.91(s) 6.09(s)	7.55-7.45(m)	7.42-7.20(m)

Conclusion:

Copper (I) halides (X = Cl, Br, I) were reacted with one mole of 4-cyanobenzaldehyde thiosemicarbazone (HL^1) and two molar Ph_3P to form complexes of general formula, [CuX(HL^1)(Ph_3P)$_2$] (X = I (**1**), Br (**2**), Cl (**3**). However, the similar reaction with HL^2 did not give the same complex with copper (I) iodide and bromide. Instead of that complexes of stoichiometry, [CuX) (Ph3P)3] X=I (**A**), Br (**B**) were formed. No ligand gets attached to copper center. Only the copper (I) chloride has formed complex of stoichiometry, [CuCl(HL^2)(Ph3P)2] **4**. Conformation of formation of complexes was done by infra-red, ultra-violet and nuclear magnetic resonance spectroscopy. All these techniques support binding of thio- ligand to copper center in neutral mode. Coordination of trihenylphosphine in these complexes is also confirmed by these techniques.

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