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Synthesis, structure and spectroscopy of mono- and di-nuclear copper(I) complexes incorporating anionic thiophene based thiosemicarbazones-first examples

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ABSTRACT

This paper reports six copper(I) complexes with a series of thiophene based N^1-substituted thiosemicarbazones, $\{(C_4H_3S)R^1C^2{=}N^3{-}N^2(H){-}C^1(=S)N^1HR^2\}$ (R^1 = H, R^2 = Me, Et, Ph, abbrev. HttscN–R^2; R^1 = CH_3; R^2 = Et, Ph, abbrev. HattscN–R^2) by reacting these thio-liands with $[Cu(OAc)(PPh_3)_2$. Here the acetate deprotonated –N^2–H hydrogen and the anionic thio-ligands have yielded mono- and di-nuclear complexes (**1**–**6**). For R^1 = H at C^2 carbon, the N^3, S-chelated complexes, $[Cu(\kappa^1N^3, \kappa^1S$–ttscN–$R^2)(PPh_3)_2]$ (R^2 = Me **1**; Et, **2**; Ph **3**) were formed in methanol. For R^1 = Me, the N^3, S-chelated-cum-sulfur bridged (κ^1N^3, κ^2S) dinuclear complexes, namely, $[Cu_2(\kappa^1N^3,\kappa^2S$–attscN–$R^2)_2(PPh_3)_2]$ (R^2 = Et **5**, Ph **6**) were obtained in CH_2Cl_2–CH_3OH. In one case for R^1 = H and with R^2 = Me, a dinuclear complex, $[Cu_2(\kappa^1N^3,\kappa^{2-}$S–ttscN–Me$)_2(PPh_3)_2]$ **4** similar to **5/6** has been isolated in CH_2Cl_2–CH_3OH. The Cu_2S_2 cores of dimers form parallelograms with the Cu···Cu distances in the range, 2.668–2.774 Å which are less than twice the sum of van der Waals radius of Cu, 2.80 Å. Complexes **1**–**6** represent first examples in the domain of thiophene based anionic thiosemicarbazones in which the thio-ligands satisfy the primary valency and bind in N,S-chelation mode (**1**–**3**) or N,S-chelation-cum-S-bridging mode (**4**–**6**).

1. Introduction

Thiosemicarbazones $\{R^1R^2C^2 = N^3{-}N^2(H){-}C^1(=S)N^1R^3R^4\}$ constitute an important class of N,S-donor thio-ligands used for the synthesis and structures of several metal complexes and interest in this area of coordination chemsitry is attributed to their analytical chemistry (ion sensors), catalysis, extraction properties and pharmacological applications [1–31]. Due to our interest in the metal-thiosemicarbazone chemistry [1], copper(I) halide chemistry of these thio-ligands has been intensively investigated [14–31]. Thiosemicarbazones as neutral ligands have shown different coordination modes in their bonding to Cu^I and have formed mononuclear [14–16,18,20–23,25,26,29,30], dinuclear [15–17,20,21,24,27–31] and polynuclear complexes [19].

The coordination chemistry of Cu^{II} with thiosemicarbazones as anions is well established [1–3], but in literature there are a few reports on Cu^I or mixed valent Cu^I/Cu^{II} complexes which contain mono- or di-anions of salicylaldehyde thiosemicarbazone, ferrocenealdehyde thiosemicarbazone [9], acyclic and cyclic derivatives of methylpyruvate thiosemicarbazones [10] satisfying the primary valenecy in addition to binding to the metal center in different coordination modes [9,10]. Thus it was believed that developing Cu^I chemistry further with anionic thiosemicarbazones might be useful in view of keen interest of chemists in investigating biological chemistry of copper(II) with anionic thiosemicarbazones [3] and knowledge of coordination chemistry of the metal in two different oxidation states might provide basis for understanding the mechanistic aspects of the biological activity.

Recently reaction chemistry of copper(I) halides was carried out with thiophene based N^1-substituted thiosemicarbazones (Chart 1), which yielded complexes having neutral thio-ligands in different coordination modes (Chart 2), namely, mode A [30], mode B [20], mode C [26], mode D [30], mode E [30], mode F [23,29] and mode G [28]. It was thought worthwhile to use the starting precursor, $Cu(OAc)(PPh_3)_2$, in which the acetate anion was believed to deprotonate a thiosemicarbazone, particularly the imino (–N^2H) hydrogen and the acetate itself leave the reaction system as acetic acid unlike the halides which remain bonded to Cu(I). Chart 1 shows various thiophene based thiosemicarbazones used in the present study, which are expected to act as anions.

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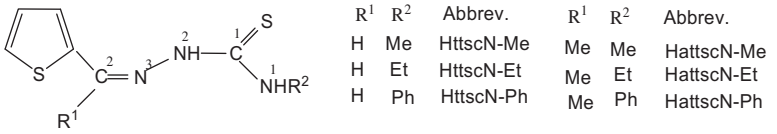


Chart 1. Various thio-ligands.

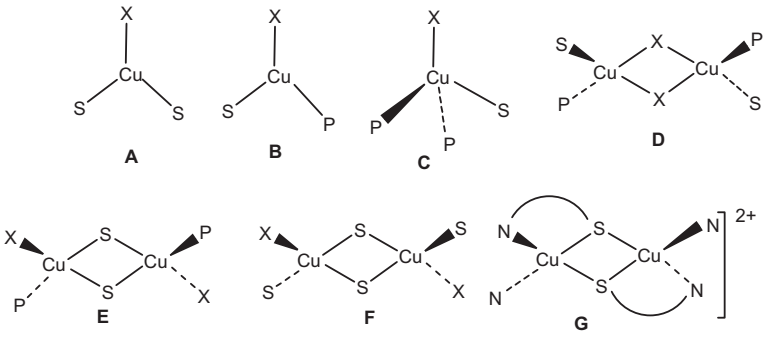


Chart 2. Modes of coordination of thio-ligands.

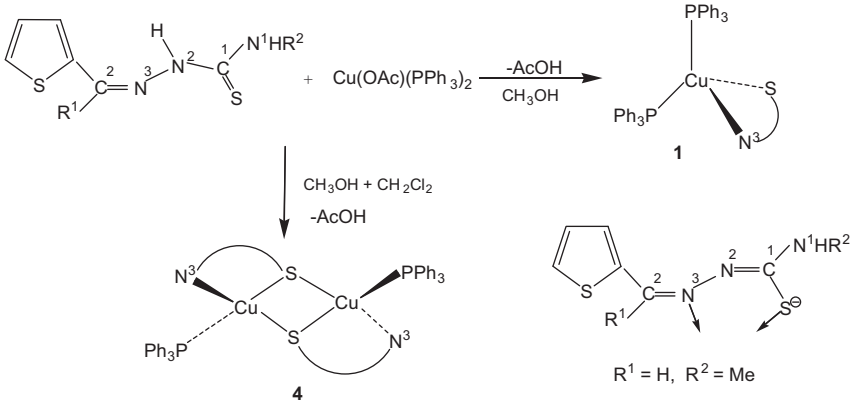
2. Materials and techniques

Copper(II) acetate monohydrate $Cu(OAc)_2{\cdot}H_2O$, *N*-methyl thiosemicarbazide, *N*-ethyl thiosemicarbazide, *N*-phenylthiosemicarbazide, triphenylphosphine, thiophene-2-carbaldehyde, and 2-acetylthiophene-2-carbaldehyde were procured from Aldrich Sigma Ltd. The thio-ligands were prepared by the condensation of thiophene-2-carbaldehyde/2-acetylthiophene-2-carbaldehyde with a respective thiosemicarbazide as previously reported [1,29,30,32]. $[Cu(OAc)(PPh_3)_2]$ was prepared by reacting copper(II) acetate with fourfold excess of triphenylphosphine (PPh_3) [10b]. The elemental analysis for C, H, and N were carried out with a thermoelectron FLASHEA1112 analyzer. The melting points were determined with a Gallenkamp electrically heated apparatus. The IR spectra of compounds were recorded in 4000–450 cm^{-1} region with a Perkin Elmer FT-IR Spectrometer by making their KBr pellets. The ^1H NMR spectra were recorded on a JEOL AL300 FT spectrometer at 300 MHz in $CDCl_3$ with TMS as the internal reference.

2.1. Synthesis of complexes

2.1.1. Synthesis of $[Cu(\kappa^1N^3,\kappa^1S\text{–}ttscN\text{–}Me)(PPh_3)_2]$ (**1**)

To a solution of HttscN–Me (0.006 g, 0.002 mmol) in CH_3OH (15 mL), $Cu(OAc)(PPh_3)_2$ (0.015 g, 0.002 mmol) was added. A pale yellow solution was obtained. Slow evaporation of this solution yielded yellow crystals. Yield, 70%, m.p. 218–220 °C. *Anal.* Calc. for $C_{43}H_{38}CuN_3P_2S_2$: C, 65.67; H, 4.87; N, 5.34; S, 8.15. Found: C, 65.39; H, 4.69; N, 5.08; S, 8.11%. I.R data (KBr pellets, cm^{-1}): $\nu(N^1\text{–}H)$, 3434sb; ν(C–H), 3047m, 2926w, 2856w; $\nu(C{=}N) + \nu(C{=}C) + \delta$(C–H), 1585m, 1508s, 1480s, 1435s; 1342m, 1319w, 1283w, 1242s, 1188w; $\nu(P\text{–}C_{Ph})$, 1092s; ν(C–N), 1028 m; 999w; ν(C–S) 744s; 695s, 617w, 509s. ^1H NMR ($CDCl_3$, δ ppm): 7.51 (d, 1H, C^6H), 7.26–7.40 (m, 34H, $C^4H + C^2H + 6Ph + N^1H + CHCl_3$), 7.11



Scheme 1. Schematic formation of a mononuclear **1** and dinuclear **4** complexes.