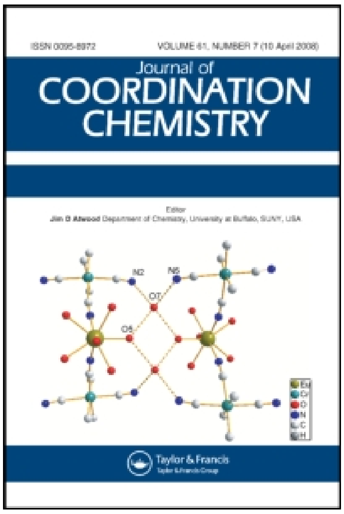

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Metal derivatives of thiosemicarbazones: crystal structure of [chloro bis(triphenylphosphino) (thiophene-2-carbaldehyde thiosemicarbazone) copper(I)] complex

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To cite this Article Lobana, Tarlok S. , Sharma, Rekha and Sharma, Roohi(2009) 'Metal derivatives of thiosemicarbazones: crystal structure of [chloro bis(triphenylphosphino) (thiophene-2-carbaldehyde thiosemicarbazone) copper(I)] complex', Journal of Coordination Chemistry, 62: 9, 1468 — 1475

To link to this Article: DOI: 10.1080/00958970802617593

URL: http://dx.doi.org/10.1080/00958970802617593

Journal of Coordination Chemistry
Vol. 62, No. 9, 10 May 2009, 1468–1475

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Metal derivatives of thiosemicarbazones: crystal structure of [chloro bis(triphenylphosphino) (thiophene-2-carbaldehyde thiosemicarbazone) copper(I)] complex

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(*Received 2 July 2008; in final form 1 August 2008*)

Reactions of copper(I) halides ($X = \mathrm{Cl, Br, I}$) with thiophene-2-carbaldehyde thiosemicarbazone and triphenylphosphine in 1 : 1 : 2 molar ratio yield tetrahedral mononuclear complexes, $[\mathrm{Cu}X(\eta^1\text{-S-Httsc})(\mathrm{Ph_3P})_2]$ ($X = \mathrm{Cl}$, **1**; Br, **2**; I, **3**), characterized by elemental analysis, IR, NMR (^{1}H, ^{13}C, ^{31}P), and single crystal X-ray crystallography (**1**). The unit cell of **1** has two independent distorted tetrahedral molecules (**1a** and **1b**) with different bond parameters. One acetonitrile is entrapped between them. Crystal data: $C_{86}H_{77}Cl_2Cu_2N_7P_4S_4$ **1**: triclinic, P-1, $a = 12.8810(9)$, $b = 18.5049(13)$, $c = 18.7430(13)$ Å, $\alpha = 63.7130(10)$, $\beta = 89.0960(10)$, $\gamma = 85.5010(10)°$, $V = 3992.4(5)$ Å^3, $Z = 2$, $R_{(\mathrm{int})} = 0.0314$. Bond parameters: **1a**, Cu(1A)–Cl(1A), 2.3803(5); Cu(1A)–S(1A), 2.3822(5); Cu(1A)–P(1A), 2.2498(5) Å; P(1A)–Cu(1A)–P(2A), 124.294(19)°; **1b**, Cu(1B)–Cl(1B), 2.3975(5); Cu(1B)–S(1B), 2.3756(5); Cu(1B)–P(1B), 2.2777(5) Å; P(1B)–Cu(1B)–P(2B), 127.156(19)°.

Keywords: Copper(I); Thiophene-2-carbaldehyde; Thiosemicarbazone; Complexes; Mononuclear

1. Introduction

Thiosemicarbazones are versatile N, S-donor ligands which form transition metal complexes of structural diversity [1–5] and have shown variable bonding properties [6] and ion-sensing ability [7–10]. Thiophene-2-carbaldehyde thiosemicarbazone (Httsc, I), one of the simplest ligands, forms mono- and di-nuclear complexes with transition and main group metals [11–20]. Chart 1 depicts different bonding modes of Httsc in its complexes. As a neutral ligand, it has η^1-S (A) [15] and μ-S (B) [16] modes and as an anionic ligand, N^3, S-chelation (C) [13], N^2, S-chelation (D) [12] and N^3, S-chelation with S-bridging (E) modes [17].

We have reported that thiophene-2-carbaldehyde thiosemicarbazone with copper(I) halides (I, Br, Cl) in 1 : 1 : 1 molar ratio (M : Ligand : $\mathrm{Ph_3P}$) form two types of dimeric complexes: iodo-bridged dimer, $[\mathrm{Cu_2}(\mu\text{-I})_2(\eta^1\text{-S-Htssc})_2(\mathrm{Ph_3P})_2]$, and S-bridged dimers, $[\mathrm{Cu_2}(\mu\text{-S-Httsc})_2(\eta^1\text{-Br})_2(\mathrm{Ph_3P})_2]\cdot 2\mathrm{H_2O}$ and $[\mathrm{Cu_2}(\mu\text{-S-Httsc})_2(\eta^1\text{-CI})_2(\mathrm{Ph_3P})_2]\cdot 2\mathrm{CH_3CN}$ [15, 16]. In this article, we report synthesis of mononuclear

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970802617593

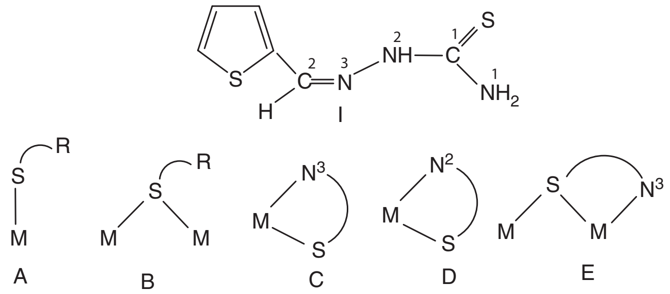


Chart 1. Bonding modes of Httsc.

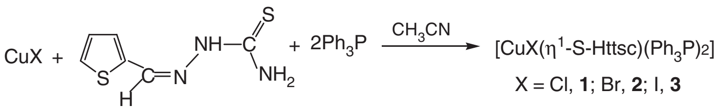
copper(I) halide complexes with Httsc which are characterized by elemental analysis, IR, and NMR spectroscopy (^{1}H, ^{13}C, ^{31}P), and X-ray crystallography (**1**).

2. Experimental

Copper(I) halides were prepared by reduction of $CuSO_4 \cdot 5H_2O$ using SO_2 in the presence of NaX ($X = $ Cl, Br, I) in distilled water [21]. Thiophene-2-carbaldehyde and Ph_3P were purchased from Aldrich Sigma Ltd. Thiosemicarbazone ligand was prepared by condensation of thiophene-2-carbaldehyde with thiosemicarbazide. Elemental analyses for C, H, and N were carried out using a thermoelectron FLASHEA1112 analyzer. Melting points were determined with a Gallenkamp electrically heated apparatus. The IR spectra of the ligands and the complexes were recorded from 4000 to 200 cm^{-1} (using KBr pellets) on a FTIR-SHIMADZU 8400 Fourier Transform spectrophotometer and on a Pye–Unicam SP-3-300 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL AL300 FT spectrometer at 300 MHz in $CDCl_3$ with TMS as the internal reference. The ^{13}C NMR spectrum of **1** was recorded at a frequency of 75.45 MHz using $CDCl_3$ as solvent and TMS as internal reference. ^{31}P NMR spectra were recorded at 121.5 MHz with $(CH_3O)_3P$ as the external reference taken as zero.

2.1. *Synthesis of [CuCl(η^1-S-Httsc)(Ph$_3$P)$_2$] (1)*

To a solution of CuCl (0.025 g, 0.252 mmol) in 20 mL of acetonitrile was added solid Httsc (0.046 g, 0.252 mmol) and the reaction mixture was stirred for 3–4 h. To this was added solid Ph_3P (0.132 g, 0.504 mmol) and stirred for 5–10 min. The clear yellow solution was filtered and kept for crystallization at room temperature. Yield: 80%; m.p. 136–138°C. Found: C, 62.5; H, 5.33; N, 5.19. $C_{42}H_{37}CuClN_3P_2S_2$, Calcd: C, 62.37; H, 4.35; N, 5.19. Main IR peaks (KBr, cm^{-1}), ν(N–H), 3400 s, 3288 s, 3124 m (–NH–), ν(C–H), 2951 b; $\delta NH_2 + \nu(C{=}N) + \nu(C{-}C)$, 1585 m, 1556 m, 1431 s; $\nu(P{-}C_{Ph})$, 1094 s; (C=S) + ν(C–N), 1043 s, 1026 s, 831 s (thioamide moiety). ^{1}H NMR ($CDCl_3$, δ ppm): 12.09 s(N^{2}H), 8.32 s(C^{2}H), 7.70 m (C^4, ^{6}H), 7.22–7.45 m (Ph_3P), 7.05 dd (C^{5}H), 6.83 sb, 5.97 sb (N^{1}H$_2$). ^{13}C NMR data (δ, ppm; J, Hz, $CDCl_3$): 175.1(C^1), 141.2(C^2), 138.2(C^3), 131.4(C^6), 127.8(C^4), 128.6(C^5), 134.0(*i*-C, $J_{P\text{–}C}$, 22.9, PhP), 133.9(*o*-C, $J_{P\text{–}C}$, 14.9, PhP), 128.3(*m*-C, $J_{P\text{–}C}$, 8.6, PhP), 129.2(*p*-C, PhP). ^{31}P NMR ($CDCl_3$, δ ppm): −111.7. Complexes **2** and **3** were prepared by a similar method.



Scheme 1. Reaction Scheme.

2.2. *Synthesis of [CuBr(η^1-S-Httsc)(Ph$_3$P)$_2$] (2)*

Yield: 85%; m.p. 190–192°C. Found: C, 59.6; H, 4.20; N, 4.63. $C_{42}H_{37}CuBrN_3P_2S_2$, Calcd: C, 59.1; H, 4.30; N, 4.92. Main IR peaks (KBr, cm^{-1}), ν(N–H), 3400 s, 3302 m, 3117 s (–NH–), ν(C–H), 2995 b; $\delta NH_2 + \nu(C{=}N) + \nu(C–C)$, 1585 s, 1549 s, 1474 s; $\nu(P–C_{Ph})$, 1094 s; $\nu(C{=}S) + \nu(C–N)$, 1088 b, 1026 s, 831 s (thioamide moiety). ^{1}H NMR ($CDCl_3$, δ ppm): 12.09 s (N^2H), 8.32 s (C^2H), 7.22–7.45 m (Ph_3P, C^4, ^6H), 7.06 dd (C^5H), 6.81 sb, 5.96 sb (N^1H_2). ^{31}P NMR ($CDCl_3$, δ ppm): −112.51.

2.3. *Synthesis of [CuI(η^1-S-Httsc)(Ph$_3$P)$_2$] (3)*

Yield: 75%; m.p. 218–220°C. Found: C, 56.4; H, 4.22; N, 4.95. $C_{42}H_{37}CuIN_3P_2S_2$, Calcd: C, 56.0; H, 4.11; N, 4.66. Main IR peaks (KBr, cm^{-1}), ν(N–H), 3431 s, 3281 m, 3148 s (–NH–), ν(C–H), 2991 m; $\delta NH_2 + \nu(C{=}N) + \nu(C–C)$, 1589 s, 1545 s, 1537 s; $\nu(P–C_{Ph})$, 1092 s; $\nu(C{=}S) + \nu(C–N)$, 1088 m, 1026 m, 830 s (thioamide moiety). ^{1}H NMR ($CDCl_3$, δ ppm): 11.63 s (N^2H), 8.36 s (C^2H), 7.22–7.69 m (Ph_3P, C^4, ^6H), 7.07 dd (C^5H), 6.84 sb, 6.03 sb (N^1H_2). ^{31}P NMR ($CDCl_3$, δ ppm): −113.54.

2.4. *Crystallography*

A prismatic crystal of **1** was measured on a Bruker AXS SMART APEX CCD diffractometer. Data were reduced and corrected for absorption using Smart and Saint [20]. The structures were solved by direct methods and refined by full matrix least squares based on F^2 with anisotropic thermal parameters for nonhydrogen atoms using SHELXTL (structure solution, refinement, and some molecular graphics) [20]. All nonhydrogen atoms were refined anisotropically and all hydrogen atoms were placed in calculated positions and refined with an isotropic displacement parameter 1.5 (methyl) or 1.2 times (all others) that of the adjacent carbon or oxygen.

3. Results and discussion

Reactions of copper(I) halides ($X = Cl, Br, I$) with thiophene-2-carbaldehyde thiosemicarbazone (Httsc) and triphenylphosphine in 1 : 1 : 2 (M : L : Ph_3P) molar ratio in acetonitrile form monomeric complexes, [CuX(η^1-S-Httsc)(Ph_3P)$_2$] **1**–**3** (X = Cl, **1**; Br, **2**; I, **3**) (scheme 1). As reported earlier, 1 : 1 : 1 molar ratio (M : L : Ph_3P) yielded only dinuclear complexes [15, 16]. Thus, reactions of copper(I) halides with thiophene-2-carbaldehyde thiosemicarbazone yield mononuclear and dinuclear complexes.

Table 1. Important bond parameters of **1**.

Parameters	**1**
Empirical formula	$C_{86}H_{77}Cl_2Cu_2N_7P_4S_4$
M	1658.65
T(K)	100(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
Units of dimensions (Å, °)	
a	12.8810(9)
b	18.5049(13)
c	18.7430(13)
α	63.7130(10)
β	89.0960(10)
γ	85.5010(10)
V (Å^3)	3992.4(5)
Z	2
D_{Calcd} (g cm^{-3})	1.380
μ(mm^{-1})	0.835
Reflections collected	24068
Unique reflns.	19759 ($R_{int} = 0.0314$)
R indices	$R = 0.0564$, $wR = 0.1144$

Complexes **1**, **2**, and **3** are stable in air and moisture and soluble in CH_3CN and $CHCl_3$. Bands due to ν(N–H) in **1**–**3** are in two regions, (i) bands between 3431 and 3280 cm^{-1} (due to NH_2 group); (ii) a broad band between 3147 and 3116 cm^{-1} (due to –N^2H group) {free ligand, 3415–3235 cm^{-1} (N^1H_2), 3150 cm^{-1} (N^2H)}. The presence of both these bands supports coordination of neutral ligand to copper. Bands due to $\delta(NH_2)$ and ν(C=N) show shifts to higher frequency in complexes (see experimental section). The characteristic ν(C=S) band at 831 cm^{-1} shifts to lower energy in **1**–**3** (free ligand, 837 cm^{-1}). This shift reveals coordination of Httsc to the metal center via thione sulfur. The characteristic band due to $\nu(P–C_{Ph})$ in the region 1091–1093 cm^{-1} supports the presence of Ph_3P in the complexes.

3.1. *Crystal structures*

The crystallographic data and bond parameters of **1** are given in tables 1 and 2. The molecular structure with numbering scheme is shown in figure 1. Complex **1** crystallized in triclinic crystal system with space group $P\bar{1}$. Two independent molecules, **1a** and **1b**, with different bond parameters crystallized in the same unit cell with one acetonitrile molecule as a solvent of crystallization. Copper is coordinated to thione S, chloride, and two P atoms. The terminal Cu–S distances {2.3822(5) Å **1a**; 2.3756(5) Å **1b**} are longer than the terminal Cu–S distance, 2.3505(9) Å in the dimer, $[Cu_2(\mu\text{-}I)_2(\eta^1\text{-S-Httsc})_2(Ph_3P)_2]$ (**4**), but close to 2.4063(6) Å in a similar type of tetrahedral complex, $[CuCl(\eta^1\text{-S-Hpytsc})(Ph_3P)_2]$ (**5**) (Hpytsc = pyridine-2-carbaldehyde thiosemicarbazone) [15]. The Cu–Cl bond distances {2.3803(5) Å **1a**; 2.3975(5) Å **1b**} are close to 2.4097(6) Å in **5**, or 2.3892(6) Å in $[CuCl(\eta^1\text{-S-H}_2\text{itsc})(Ph_3P)_2]$ (**6**) (H_2itsc = isatin-3-thiosemicarbazone) [22], but longer than 2.3392(5) Å in $[Cu_2Cl_2(\mu\text{-S-Httsc})_2(Ph_3P)_2]$ (**7**) [16]. The Cu–Cl bond distances are less than the sum of the ionic radii of Cu and Cl, 2.58 Å [21]. The Cu–P bond distances are close to the literature values [15, 16].

Table 2. Bond lengths (Å) and angles (°) of **1**.

$[CuCl(\eta^1\text{–S–Httsc})(Ph_3P)_2]$ **1**			
Cu(1A)–S(1A)	2.3822(5)	S(1A)–C(37A)	1.7094(19)
Cu(1B)–S(1B)	2.3756(5)	S(1B)–C(1B)	1.701(2)
Cu(1A)–Cl(1A)	2.3803(5)	C(37A)–N(1A)	1.328(2)
Cu(1B)–Cl(1B)	2.3975(5)	C(37B)–N(1B)	1.328(3)
Cu(1A)–P(1A)	2.2498(5)	C(37A)–N(2A)	1.331(2)
Cu(1B)–P(1B)	2.2777(5)	C(37B)–N(2B)	1.334(3)
S(1A)–Cu(1A)–Cl(1A)	114.591(18)	S(1A)–Cu(1A)–P(1A)	107.739(18)
S(1B)–Cu(1B)–Cl(1B)	108.951(18)	S(1B)–Cu(1B)–P(1B)	108.972(19)
P(1A)–Cu(1A)–Cl(1A)	103.933(18)	Cu(1A)–S(1A)–C(37A)	107.69(6)
P(2A)–Cu(1A)–Cl(1A)	104.302(19)	Cu(1B)–S(1B)–C(37B)	110.83(2)
P(1B)–Cu(1B)–Cl(1B)	101.713(19)	P(1A)–Cu(1A)–P(2A)	124.294(19)
P(2B)–Cu(2B)–Cl(2B)	109.3031(19)	P(1B)–Cu(1B)–P(2B)	127.156(19)

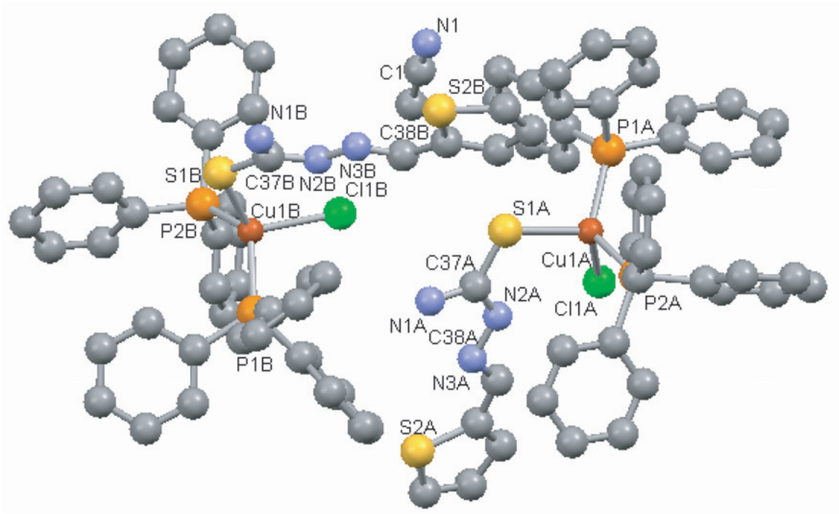
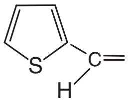
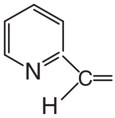
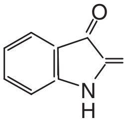


Figure 1. Structure of $[CuCl(\eta^1\text{-S-Httsc})(Ph_3P)_2]$ (**1**) with numbering scheme.

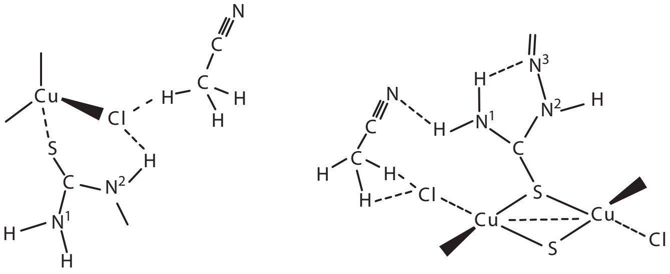
Bond angles around copper lie in the range 103.93–124.29° **1a** and 101.713–127.156° **1b** in a highly distorted tetrahedral geometry with more distortion in **1b**. The Cu–S–C bond angles, 107.69(6)° **1a** and 110.83(2)° **1b**, are close to that in **7**. A comparison of important bond lengths and bond angles of tetrahedral complexes are given in table 3. The S atom is bonded more strongly in complex **6** than in **1** or **5** due to the ketonic substituents (i.e., isatin) in **6** than five- or six-member heterocyclic rings (thiophene **1**, or pyridine **5**). The same trend is followed in C–S bond. The Cu–S–C angle is maximum in **6** and minimum in **5**. The larger Cu–S–C bond angle in **6** is due to the bulkier isatin ring, which causes steric hindrance. The P–Cu–P angle is exceptionally large in **1b** and normal in **1a**.

In **1**, the imino hydrogen forms weak intramolecular hydrogen bonds with chloride (scheme 2), $N^2H\cdots Cl$, 3.152 Å, absent in $[Cu_2Cl_2(\mu\text{-S-Httsc})_2(Ph_3P)_2]$ [16]. No intermolecular hydrogen bonding is present in **1**, only a weak hydrogen bond between methyl hydrogen of acetonitrile and chloride, $\{NCCH_2H\cdots Cl, 2.958\,Å\}$ in **1a**, which was relatively stronger $\{NCCHH_2\cdots Cl, 2.62, 2.79\,Å\}$ in **6**.

Table 3. A comparison of important bond lengths and angles of some tetrahedral complexes.[a]

Complex	[CuCl(Httsc)(Ph$_3$P)$_2$] **1** (this work)	[CuCl(Hpytsc)(Ph$_3$P)$_2$] **5** [15]	[CuCl(H$_2$itsc)(Ph$_3$P)$_2$] **6** [22]
R^1			
Cu–Cl	2.3975(5)	2.4097(6)	2.3892(6)
Cu–S	2.3756(5)	2.4063(6)	2.3323(5)
Cu–P	2.2777(5)	2.2621(6)	2.2621(5)
S–C	1.701(2)	1.705(2)	1.6811(18)
P–Cu–P	127.156(19)	120.92	121.763(19)
Cu–S–C	110.83(2)	103.13(8)	112.14(6)

Note: [a]R^1 = N–NH–C(=S)NH$_2$.



1

6 [16]

Scheme 2. Intramolecular H-bonding.

The stoichiometry of **2** and **3** suggests tetrahedral structures for these complexes similar to that of **1**.

3.2. *NMR spectroscopy*

The ^{1}H NMR spectra of **1**–**3** showed N^{2}H proton signal at 12.65, 12.09, and 11.62 ppm, respectively, downfield shifted vis-à-vis the free ligand (δ 9.45 ppm), indicating that deprotonation does not occur during complexation. Due to the restricted rotation about C–N, the N^{1}H$_2$ protons gave two broad signals between 6.02–5.96 ppm and 6.84–6.80 ppm in **1**–**3** and shifted upfield from the free ligand (δ 6.30, 7.17 ppm). The ring protons of Ph$_3$P are multiplets in the range δ 7.21–7.45 ppm.

In the ^{13}C spectrum of **1**, C^1 is at high field, δ 175.1 ppm and C^2 at low field, δ 141.1 ppm vis-à-vis free ligand (δ 177.7 ppm and δ 137.7 ppm, respectively). The ligand ring carbon atoms show mixed behavior; ring carbons of Ph$_3$P (*i*-C, *o*-C, *m*-C) were clearly resolved. The *p*-C appeared as a sharp singlet at δ 129.2 ppm.

Each complex showed a singlet at δ −111.7 ppm (**1**), δ −112.5 ppm (**2**) and δ −113.5 ppm (**3**) in their ^{31}P spectra, close to free Ph$_3$P (δ −113.15 ppm), similar to mononuclear copper(I) complexes of thiosemicarbazones [16]. Coordination shifts ($\Delta\delta = \delta_{\text{complex}} - \delta_{\text{ligand}}$) are: 1.427, 0.637, and −0.39 ppm, respectively.

4. Conclusion

Thiophene-2-carbaldehyde thiosemicarbazone yields mononuclear **1–3** and dinuclear $[Cu_2X_2(Ph_3P)_2(Httsc)_2]$ ($X = Cl, Br, I$) complexes in acetonitrile [15, 16]. This behavior is unlike that shown by pyridine-2-carbaldehyde thiosemicarbazone, isatin-3-thiosemicarbazone, and benzophenone thiosemicarbazone for which only mononuclear complexes could be isolated as crystalline compounds [15, 22, 23]. It is possible that dinuclear complexes of the latter ligands, if formed in acetonitrile have low solubility and do not give crystals and thus in the presence of two moles of organo-phosphorus ligand mononuclear complexes get preferentially crystallized.

Supplementary material

Full details have been deposited with the Cambridge Crystallographic Data Centre, CCDC for **1** is 692990. 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; Email: deposit@ccdc.cam.ac.uk; or http://www.ccdc.cam.ac.uk).

Acknowledgments

Financial assistance from UGC (Scheme No.: 12-92/2001 (SR-I)), New Delhi, is gratefully acknowledged. The authors thank Dr Matthias Zeller of Youngstown State University, USA, for help in X-ray crystallography.

References

[1] (a) M.J.M. Campbell. *Coord. Chem. Rev.*, **15**, 279 (1975); (b) S.B. Padhye, G. Kauffman. *Coord. Chem. Rev.*, **63**, 127 (1985).
[2] D.X. West, S.B. Padhye, P.B. Sonawane. *Struct. Bonding* (Berlin Ger.), **76**, 4 (1991).
[3] D.X. West, A.E. Liberta, S.B. Padhye, R.C. Chikate, P.B. Sonawane, A.S. Kumbhar, R.G. Yerande. *Coord. Chem. Rev.*, **123**, 49 (1993).
[4] J.S. Casas, M.S. Garcia-Tasende, J. Sordo. *Coord. Chem. Rev.*, **209**, 197 (2000).
[5] D.R. Smith. *Coord. Chem. Rev.*, **164**, 575 (1997).
[6] T.S. Lobana, S. Khanna, R. Sharma, G. Hundal, R. Sultana, M. Chaudhary, R.J. Butcher, A. Castineiras. *Cryst. Growth Des.*, **8**, 1203 (2008).
[7] R.K. Mahajan, I. Kaur, T.S. Lobana. *Talanta*, **59**, 101 (2003).
[8] R.K. Mahajan, I. Kaur, T.S. Lobana. *Ind. J. Chem.*, **45A**, 639 (2006).
[9] R.K. Mahajan, T.P.S. Walia, Sumanjit, T.S. Lobana. *Talanta*, **67**, 755 (2005).
[10] L.S. Sarma, J.R. Kumar, C.J. Kumar, A.V. Reddy. *Anal. Lett.*, **36**, 605 (2003).
[11] W.-S. Hong, C.-Y. Wu, C.-S. Lee, W.-S. Hwang, M.Y. Chiang. *J. Organomet. Chem.*, **689**, 277 (2004).
[12] T.S. Lobana, G. Bawa, A. Castineiras, R.J. Butcher. *Organometallics*, **27**, 175 (2008).

[13] J. Garcia-Tojal, J.L. Pizarro, A. Garcia-Orad, A.R. Perez-Sanz, M. Ugalde, A.A. Diaz, J.L. Serra, M.I. Arriortua, T. Rojo. *J. Inorg. Biochem.*, **86**, 627 (2001).

[14] C.G. Suresh, A. Deshpande, S.S. Tavale, P. Umapathy. *J. Crystallogr. Spectrosc. Res.*, **21**, 485 (1991).

[15] T.S. Lobana, Rekha, R.J. Butcher, A. Castineiras, E. Bermejo, P.V. Bharatam. *Inorg. Chem.*, **45**, 1535 (2006).

[16] T.S. Lobana, Rekha, A.P.S. Pannu, G. Hundal, R.J. Butcher, A. Castineiras. *Polyhedron*, **26**, 2621 (2007).

[17] (a) R.D. Pike, A.B. Wiles, T.A. Tronic. *Acta Cryst.*, **E62**, m2992 (2006); (b) W. Kaim, J. Rall. *Angew. Chem. Int. Ed. Engl.*, **35**, 43 (1996); (c) R.J. Haines, R.E. Wittrig, C.P. Kubiak. *Inorg. Chem.*, **33**, 4723 (1994); (d) J. Anekwe, A. Hammerschmidt, A. Rompal, B. Krebs. *Z. Anorg. Allg. Chem.*, **632**, 1057 (2006); (e) E.I. Solomon, U.M. Sundaram, T.E. Machonkin. *Chem. Rev.*, **96**, 2563 (1996); (f) K. Singh, J.R. Long, P. Stavropoulos. *Inorg. Chem.*, **37**, 1073 (1998); (g) H. Araki, K. Tsuga, Y. Sasaki, S. Ishizaka, N. Kitamura. *Inorg. Chem.*, **46**, 10032 (2007); (h) H.V.R. Dias, H.V.K. Diyabalanage, M.G. Eldabaga, O. Elbjeirama, M.A. Rawashdeh-Omary. *J. Am. Chem. Soc.*, **127**, 7489 (2005).

[18] J. Garcia-Tojal, A. Garcia-Orad, J.L. Serra, J.L. Pizarro, L. Lazama, M.I. Arriortua, T. Rojo. *J. Inorg. Biochem.*, **75**, 45 (1999).

[19] T.S. Lobana, A. Sanchez, J.S. Casas, A. Castineiras, J. Sordo, M.S. Garcia-Tasende. *Main Group Met. Chem.*, **24**, 61 (2001).

[20] (a) S.-G. Teoh, S.-H. Ang, H.-K. Fun, C.-W. Ong. *J. Organomet. Chem.*, **580**, 17 (1999); (b) Bruker, SMART, SAINT and XREP, Area Detector Control and Data Integration and Reduction Software, Bruker Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA (1995). (c) G.M. Sheldrick. SHELXL-97, Program for Refinement of Crystal Structures, University of Gottingen, Gottingen, Germany (1997).

[21] (a) J.E. Huheey, E.A. Keiter, R.L. Keiter. *Inorganic Chemistry: Principals of Structure and Reactivity*, 4th Edn, Harper Collins College, Publishers, New York (1993); (b) G. Brauer. *Handbook of Preparative Chemistry*, 2nd Edn, Vol. 2, Academic Press, New York (1965).

[22] T.S. Lobana, Rekha, B.S. Sidhu, A. Castineiras, E. Bermejo, T. Nishioka. *J. Coord. Chem.*, **58**, 803 (2005).

[23] T.S. Lobana, S. Khanna, R.J. Butcher, A.D. Hunter, M. Zeller. *Polyhedron*, **25**, 2755 (2006).