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Synthesis, crystal structure and DFT calculations of copper(I) complex of 2-nitrobenzaldehyde-N^1-methylthiosemicarbazone

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Copper(I) halides (I, Br, Cl) reacted with 2-nitrobenzaldehyde-N^1-methylthiosemicarbazone (L = 2-NO_2-Hbtsc-N^1-Me) and triphenylphosphine in 1:1:2 (M:L:Ph_3P) molar ratio to form stoichiometric complexes, [CuX(η^1-S-2-NO_2-Hbtsc-N^1-Me)(Ph_3P)$_2$] (X = I (**1**), Br (**2**), Cl (**3**)). Formation of these complexes has been confirmed by elemental analysis, IR and ^{1}H NMR. The X-ray structure of complex **1**, showed the presence of two molecules with slightly different bond parameters. Geometry around copper(I) center is distorted tetrahedral. Two molecules are interconnected by H-bonding between imino nitrogen N(14) of one molecule and phenyl hydrogen of one of the triphenylphospine molecules of the second molecule, {H(14)N···HC, 2.701 Å, N···H–C, 156.85°) forming a H-bonded dimer. The geometry of the thione ligated copper(I) complex was optimized in gas phase by employing B3LYP/6-31G(d, p) method using Gaussian 09 software package. The optimized geometry of the copper(I) complex displays similar structure as that of the crystal structure of complex **1.**

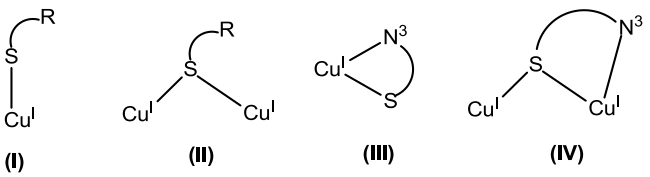
Keywords: Coordination chemistry, Crystal structures, Thiosemicarbazones, Copper, Triphenylphosphine, Tetrahedral monomers

From the last few decades, chemistry of thiosemicarbazones has received considerable attention due to their interesting bonding behavior, structural diversity, analytical and biological applications[1-18]. Copper(I) being a soft acid, preferably binds to the thione sulfur of thiosemicarbazones in different ways (Scheme 1). The various bonding modes observed for copper(I) thiosemicarbazone complexes are, η^1-terminal (**I**), μ-bridging (**II**), N^3, S-chelation (**III**) and N^3,S-chelation-cum-S-bridging (**IV**)[19-21].

Amongst the various thiosemicarbazones, the coordination chemistry of nitrobenzaldehyde thiosemicarbazone is less explored. Only few complexes of nitrobenzaldehyde thiosemicarbazone with transition metals are structurally characterized. 4-nitrobenzaldehyde thiosemicarbazone (4-NO_2-Hbtsc, H^1L) reacted with ruthenium to form octahedral complexes viz., [$Ru^1L_2(Ph_3P)_2$][22], [Ru^1L_2(2,2'-bpy)][22] and [$Ru^1LH(Ph_3P)_2$][23]. The ligand also formed a similar tetrahedral complex with cadmium, [$CdI_2(H^1L)_2$][24]. 3-Nitrobenzaldehyde thiosemicarbazone (3-NO_2-Hbtsc, H^2L) formed an ionic gold(I)–thiosemicarbazone complex, [$Au_2(H^2L)_4$]Cl_2[25]. To the best of our knowledge, no metal complex with 2-nitrobenzaldehyde thiosemicarbazone, has been structurally characterized till date. In the present study, we report the copper(I) complexes of 2-nitrobenzaldehyde-N^1-methylthiosemicarbazone (2-NO_2-Hbtsc-N^1-Me). The Copper(I) halides (X = I, Br, Cl) were reacted with 2-nitrobenzaldehyde-N^1-methylthiosemicarbazone (2-NO_2-Hbtsc-N^1-Me) and Ph_3P to yield stoichiometric complexes, [CuX(2-NO_2-Hbtsc-N^1-Me)(Ph_3P)$_2$] (X = I (**1**), Br (**2**), Cl (**3**) and characterized by elemental analysis, ^{1}H NMR and X-ray crystallography (**1**). The theoretical calculations for the lowest energy structure of complex **1** are in agreement with the experimental data.

Experimental

Potassium chloride, potassium bromide, potassium iodide, triphenylphosphine, 2-nitrobenzaldehyde, N-methylthiosemicarbazide and triphenylphosphine were procured from Loba Pvt. Ltd. Copper(I) iodide, bromide and chloride were prepared by the reduction of $CuSO_4 \cdot 5H_2O$ using SO_2 in the presence of KI, KBr and KCl in water respectively[26]. 2-Nitrobenzaldehyde-N^1-methylthiosemicarbazone was prepared by refluxing 2-nitrobenzaldehyde and N-methylthiosemicarbazide



Bonding modes of thiosemicarbazones with copper(I)

Scheme 1

in methanol for 6-8 h. C, H and N analysis was performed using a Thermoelectron FlashEA1112 CHNS analyzer. Infrared spectra were recorded in the range 4000–400 cm^{-1} on a Shimadzu FTIR 8400S spectrophotometer. Melting points were determined with an electrically heated Gallenkamp apparatus. Ultraviolet (UV) spectra were recorded on Shimadzu UV-1800 spectrophotometer. ^1H NMR were recorded on an AV500 FT spectrometer operating at a frequency of 500 MHz using $CDCl_3$ as solvent with TMS as the internal standard.

The [CuI(η^1-S-2-NO_2-Hbtsc-N^1-Me)(Ph_3P)$_2$] (**1**) complex was synthesized as follows: To a solution of CuI (0.025 g, 0.131 mmol) in 15 mL of acetonitrile, solid 2-NO_2-Hbtsc-N^1-Me (0.031 g, 0.131 mmol) was added and the reaction mixture was stirred for 3-4 h. To this, solid Ph_3P (0.069 g, 0.262 mmol) was added and stirred for 10 minutes. The yellow colored clear solution thus obtained, was filtered and left to crystallize at room temperature. Yield: 0.09 g, 72%; m.pt.: 202–204 ºC. Anal. (%): $C_{45}H_{40}N_4P_2SO_2P_2CuI$, Found: C, 56.67; H, 4.12; N, 5.81. Calcd: C, 56.69; H, 4.19; N, 5.87. IR (KBr, cm^{-1}), υ(N–H), 3464s, 3328m, 3206m; υ(-NH-), 3120m; υ(C–H_{Ph}), 3057s; δ(NH_2)+υ(C=N)+υ(C–C), 1630s, 1529s; υ(C=S) 835m (thioamide moiety), υ(P–C_{Ph}), 1093s. UV (CH_2Cl_2, nm): π→π*, 280; n→π*, 345. ^1H NMR ($CDCl_3$, δ(ppm)): 11.32s (-NH), 8.36s (C^2H), 8.09d ($C^{3'}H$), 8.02d ($C^{6'}H$), 7.32–7.42m ($C^{5'}H$+Ph_3P), 3.16d (-CH_3).

Complexes **2** and **3** were prepared in a similar manner.

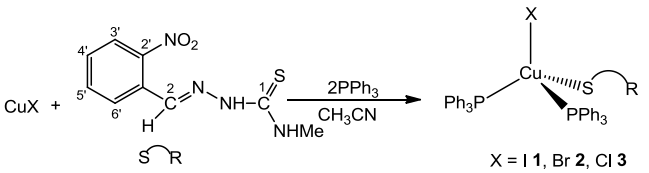
[CuBr(η^1-S-2-NO_2-Hbtsc-N^1-Me)(Ph_3P)$_2$] (**2**): Yield: 0.107 g, 68%; m.pt. 198–200 ºC. Anal. (%): $C_{45}H_{40}N_4P_2SO_2P_2CuBr$, Found: C, 59.60; H, 4.44; N, 6.15. Calcd.: C, 59.63; H, 4.41; N, 6.18; S, 3.63. IR (KBr, cm^{-1}), υ(N–H), 3472s, 3358m, 3226; υ(-NH-), 3139m; υ(C–H_{Ph}), 3037s; δ(NH_2)+υ(C=N) +υ(C–C), 1617s, 1559s; υ(C=S) 837m (thioamide moiety), υ(P–C_{Ph}), 1095s. UV (CH_2Cl_2, nm): π→π*, 286; n→π*, 346. ^1H NMR ($CDCl_3$, δ(ppm)): 11.44s (-NH), 8.32s (C^2H), 8.12d ($C^{3'}H$), 8.04d ($C^{6'}H$) 7.33–7.52m ($C^{5'}H$+Ph_3P), 3.14d (-CH_3).

[CuCl(η^1-S-2-NO_2-Hbtsc-N^1-Me)(Ph_3P)$_2$] (**3**): Yield: 0.141g, 65%; m.pt. 185–187 ºC. Anal. (%): $C_{45}H_{40}N_4P_2SO_2P_2CuCl$, Found: C, 62.73; H, 4.61; N, 6.61. Calcd.: C, 62.71; H, 4.64; N, 6.40. IR (KBr, cm^{-1}), υ(N–H), 3452s, 3348m, 3221; υ(-NH-), 3129m; υ(C–H_{Ph}), 3047s; δ(NH_2)+υ(C=N)+υ(C–C), 1619s, 1558s; υ(C=S) 839m (thioamide moiety), υ(P–C_{Ph}), 1095s. UV (CH_2Cl_2, nm): π→π*, 270; n→π*, 345. ^1H NMR ($CDCl_3$, δ(ppm)): 11.26s (-NH), 8.21s (C^2H), 8.07d ($C^{3'}H$), 8.03d ($C^{6'}H$) 7.38–7.54m ($C^{5'}H$+Ph_3P), 3.11d (-CH_3).

X-ray intensity data of 18027 reflections (of which 13365 unique) was collected on X'calibur-CCD equipped with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). A crystal of dimensions 0.3×0.2×0.2 mm was used for data collection. The cell dimensions were determined by the least-square fit of angular settings, of 17118 reflections in the θ range of 3.42°–26.00°. The intensities were measured by ω scan mode for θ range of 3.48°–24.99°. 13365 reflections were treated as observed ($I>2\sigma(I)$). Data are corrected for Lorentz, polarisation and absorption factors. The structure was solved by direct methods using ShelXS97[27]. All non-hydrogen atoms of the molecule were located in the best E-map. Full-matrix least-squares refinement was carried out using ShelXL97[28]. The final refinement cycles converged to an R = 0.0578 and wR (F^2) = 0.0849 for the observed data. Residual electron densities ranged from –0.567 to –0.544 e $Å^{-3}$.

The geometry of the thione ligated copper(I) complex was optimized in gas phase by B3LYP/ 6-31G(d, p) method using Gaussian 09 software package[29]. Additional diffuse function was applied for the phosphorus atom to include the *d* atomic orbital function[30], [P 0, D 1 1.0,0.55 0.100D+01].

The B3LYP method is a hybrid functional method which Lee *et al.*[31] improved, based on the Beche's three-parameter hybrid function with non-local correlation[32,33]. The force constants and vibrational frequencies were determined by computing the analytical frequencies at the stationary points obtained after optimization to confirm that they were true minima. The initial structure of the complex was chosen based on the crystal structure of compound **1**. To reduce the computation time, the phenyl groups of the triphenylphosphines were replaced with hydrogen atoms. The coordination environment of the central copper(I) ion remains tetrahedrally connected to two phosphorus atoms of phosphine ligand (PH_3), one iodide ion (I^-), and one sulphur atom (thione sulphur of the thiosemicarbazone ligand). To model the N^3, S- binding mode of the ligand, the initial structure was taken with copper(I) coordinated to two phosphorus atoms of the two phosphine ligands (PH_3) and one sulphur (thiol from thiosemicarbazone ligand) and nitrogen (amine from thiosemicarbazone ligand).



Synthesis of complexes **1-3**

Scheme 2

Results and discussion

The reaction sequence of synthesis of complexes **1-3** is shown in Scheme 2. The reaction of 2-nitrobenzaldehyde-N^1-methylthiosemicarbazone (2-NO_2-Hbtsc-N^1-Me) with copper(I) halides (I, Br, Cl) and triphenylphosphine in 1:1:2 (M:L:PPh_3) molar ratio yielded stoichiometric compounds, [CuX(η^1-S-2-NO_2-Hbtsc-N^1-Me)($Ph_3P)_2$] (X = I (**1**), Br (**2**), Cl (**3**)). These complexes were characterized by elemental analysis, IR, UV and ^{1}H NMR spectroscopy. Structure of complex **1** was determined using single crystal X-ray crystallography. Melting points of complexes **1-3** are found to be not only close to each other (202–204 °C **(1)**, 198–200 °C **(2)** and 185–187 °C **(3)**), but also to similar types of monomeric tetrahedral complexes of copper(I) halides with N^1-substituted pyridine thiosemicarbazones[34]. Results of elemental analysis and similar melting point data suggest that complexes **1-3** are isostructural.

The crystallographic data and important bond parameters (bond lengths and bond angles) of complex **1** are given in Tables 1 and 2 respectively. The molecular structure along with numbering scheme is given in Fig. 1. Complex **1** crystallized in triclinic crystal system with space group P-1.

The X-ray structure of complex **1** shows two molecules with slightly different bond parameters. The Cu–S bond distances are, Cu(1)–S(1) 2.3965(11) Å and Cu(2)–S(2) 2.3763(11) Å. These Cu–S distances are comparable with the tetrahedral complexes of copper(I)-thiosemicarbazones reported in literature[19]. The Cu–S bond distances are closer to the sum of covalent radii of copper and sulfur, 2.40 Å[35]. The Cu–I bond distances, Cu(1)–I(1) 2.6806(8) Å and Cu(2)–I(2) 2.7235(8) Å are less than the sum of ionic radii of Cu^+ and I^-, 2.97Å[35]. The C–S bond distances, C(2)–S(1) 1.697(3) Å, C(47)–S(2) 1.695(3) Å, are close to the C=S bond distance of 3-nitrobenzaldehyde thiosemicarbazone 1.695(3) Å and 5-hydroxy-2-nitrobenzaldehyde thiosemicarbazone, 1.664(4) Å[36,37], indicating coordination of the ligand to metal in thione form. All the Cu–P bond distances are close to literature values[19].

Bond angles around the copper center in each molecule lie in range, 106.01–122.33°, indicating

Table 1 — Crystallographic data of complex **1**

Empirical formula	$C_{45}H_{40}CuIN_4O_2P_2S$
Formula weight	953.25
Temp. (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Crystal size (mm)	0.3×0.2×0.2
Space group	P-1
Z (calc.)	4
Density (g cm^{-3})	1.451
Abs. coeff. (mm^{-1})	1.371
a (Å)	14.283(5)
b (Å)	15.868(5)
c (Å)	20.041(5)
α (°)	77.285(5)
β (°)	86.035(5)
γ (°)	80.110(5)
V ($Å^3$)	4363(2)
F(000)	1928
θ range for data collection (°)	3.42–26.50
Limiting indices	$-17 \geq h \geq 17$; $-19 \geq k \geq 19$; $-25 \geq l \geq 25$
Reflections	18027
Goodness-of- fit on F^2	1.036
[$I>2\sigma(I)$]	13365
R indices (all data)	*R1* = 0.0375; *wR2* = 0.0779
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.567, -0.544

Table 2 — Selected bond length and bond angles for complex **1**

Bond lengths (Å)			
I(1)–Cu(1)	2.6806(8)	I(2)–Cu(2)	2.7235(8)
Cu(1)–P(1)	2.2904(10)	Cu(2)–P(3)	2.2930(10)
Cu(1)–P(2)	2.3021(11)	Cu(2)–P(4)	2.2979(12)
Cu(1)–S(1)	2.3965(11)	Cu(2)–S(2)	2.3763(11)
S(1)–C(2)	1.698(3)	S(2)–C(47)	1.695(3)
C(2)–N(2)	1.349(4)	N(6)–C(47)	1.347(4)
N(2)–N(3)	1.370(4)	N(6)–N(7)	1.367(4)
Bond angles (°)			
P(1)–Cu(1)–P(2)	119.02(3)	P(3)–Cu(2)–P(4)	122.33(4)
P(1)–Cu(1)–S(1)	105.06(4)	P(3)–Cu(2)–S(2)	105.42(4)
P(2)–Cu(1)–S(1)	109.83(3)	P(4)–Cu(2)–S(2)	106.71(3)
P(1)–Cu(1)–I(1)	106.02(3)	P(3)–Cu(2)–I(2)	102.33(3)
P(2)–Cu(1)–I(1)	106.40(3)	P(4)–Cu(2)–I(2)	109.40(3)
S(1)–Cu(1)–I(1)	110.37(3)	S(2)–Cu(2)–I(2)	110.34(3)
C(2)–S(1)–Cu(1)	111.03(11)	C(47)–S(2)–Cu(2)	111.24(11)

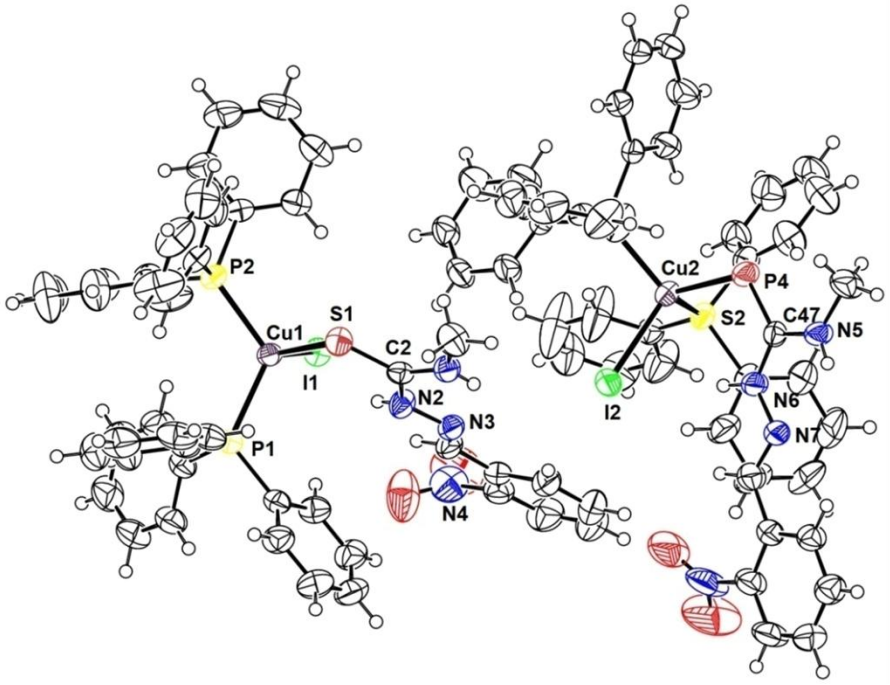


Fig. 1 — Structure of complex **1** with numbering scheme.

distorted tetrahedral geometry, with maximum distortion at P–Cu–P, {122.33 and 119.02°}. Steric bulk of two Ph_3P ligands causes maximum distortion. The Cu–S–C bond angles, i.e., {111.03(11) and 111.24(11)°} are close to 115.73(7)° in $[CuI(Hbtsc)(Ph_3P)_2]$ (Hbtsc = benzadehyde thiosemicarbazone)[19], but much larger than that in [2-PyPhHg(btsc)], {99.09(12)°}, where thiosemicarbazone ligand forms a chelate ring[38].

In complex **1**, two molecules are interconnected by H-bonding between imino nitrogen (N(14)) of one molecule and phenyl hydrogen, of one of the triphenylphospine molecules of second the molecule, {H(2)N···HC, 2.701 Å, N···H–C, 156.85°) resulting in the formation of H-bonded dimer (Fig. 2).

In complexes **1**-**3**, the ν(N-H) band due to (-NH_2) and (-NH-) groups appeared in the ranges, 3472–3206 cm^{-1} and 3139–3120 cm^{-1} respectively. Presence of these bands in the complexes suggests that 2-nitrobenzaldehyde-N^1-methylthiosemicarbazone has coordinated as a neutral ligand. The ν(C=S) band in free ligand appeared at 856 cm^{-1}. The low energy shift of ν(C=S) band in complexes, 835 cm^{-1} (**1**), 837 cm^{-1} (**2**) and 839 cm^{-1} (**3**) supports the bonding of the ligand in thione form. The coordination of Ph_3P ligand to metal center is shown by the presence of characteristic ν(P–C_{Ph}) bands in the range,

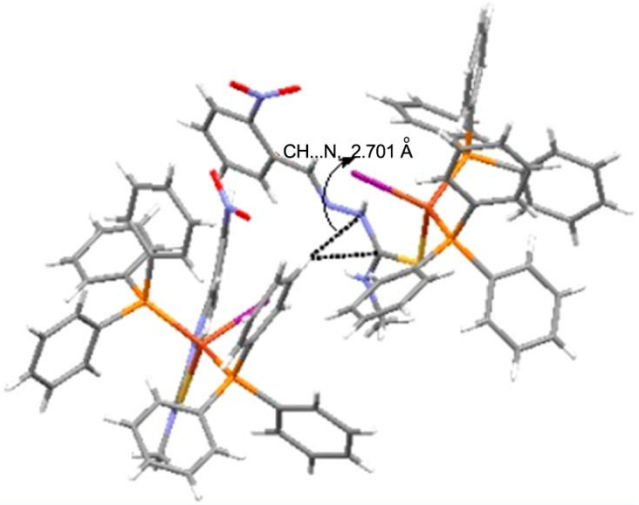


Fig. 2 — Interactions between two units forming H-bonded dimer.

1093–1095 cm^{-1} in complexes **1**-**3**. UV spectrum of free ligand shows two transitions at 293 nm and 352 nm due to π→π* and n→π* excitation respectively. These peaks show hypsochromic shift (blue shift) in complexes **1**-**3**, indicating binding of thio ligand with metal (Supplementary data, Figs 1-4).

In ^1H NMR spectra of complexes **1**-**3**, the most characteristic -NH signal appeared in range δ = 11.26–11.44 ppm. The downfield shifts of this signal in complexes **1**–**3**, vis-à-vis free ligand

Table 3 — Comparison of the bond angle (°) and bond lengths (Å) of the crystal structure of compound **1** with the optimized structure

Molecule **1**		Molecule **2**		Optimized structure	
Cu(1)–P(1)	2.290 Å	Cu(2)–P(3)	2.293 Å	Cu–P(1)	2.389 Å
Cu(1)–P(2)	2.302 Å	Cu(2)–P(4)	2.297 Å	Cu–P(2)	2.388 Å
Cu(1)–S(1)	2.396 Å	Cu(2)–S(2)	2.376 Å	Cu–S	2.489 Å
Cu(1)–I(1)	2.680 Å	Cu(2)–I(2)	2.723 Å	Cu-I	2.720 Å
Avg. torsion angle NO_2 – Ph ring	39.67°	Avg. torsion angle NO_2 – Ph ring	40.95°	Avg. torsion angle NO_2 – Ph ring	64.22°

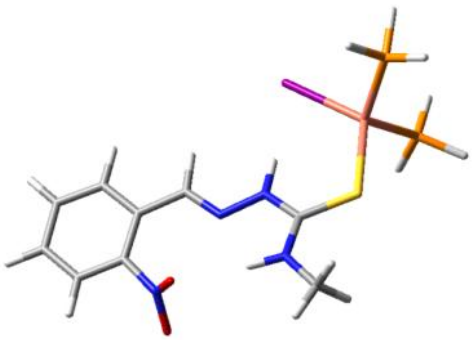


Fig. 3 — Optimized geometry of [CuI(2-NO_2-Hbtsc-N^1-Me)(PH_3)$_2$].

(δ = 10.56 ppm), supported the coordination of ligands to a metal center. Presence of -NH signal ensured that no deprotonation occurred during complexation. The C^2H signal in free ligand at δ = 8.06 ppm, showed downfield shift in the complexes **1**-**3** {δ = 8.21–8.36 ppm}. The NHMe proton was obscured by ring protons of Ph_3P, which appeared in the range, δ = 7.32–7.42 ppm in complexes **1**-**3**. The methyl protons of -$NHCH_3$ appeared as doublet in the range, δ = 3.11–3.16 ppm in **1**-**3**.

Theoretical modeling studies were also carried out. The optimized geometry of the copper(I) complex displays certain similarities with the crystal structure of complex **1** (Fig. 3). In the unit cell of the crystal structure, two molecules are present. The bond lengths around the copper metal are given in Table 3 and are comparable to the data obtained from the optimized structure. The Cu–I bond length values match well for all the structures, but the Cu–P and Cu–S bond lengths are longer than the corresponding values observed in the crystal structure.

The nitro group attached to the phenyl ring in the *ortho* position is not in the same plane of the phenyl ring as expected for a resonance stabilized structure due to the steric strain of the N-Me group in both the crystals and the optimized structures. Attempts to optimize the structure of the complex with N^3, S- mode of the thiosemicarbazone ligand along with two phosphine (PH_3) ligands were unsuccessful, signifying that copper(I) complexes of the thiosemicarbazone ligands in the N^3,S-chelation mode are unstable. This observation has also been corroborated by the fact that only a few copper(I) complexes have been reported in the literature with N^3, S- bound thiosemicarbazone ligands along with two phosphine ligands[38].

In the present study, synthesis and characterization of copper(I) complexes of 2-nitrobenzaldehyde-N^1-methylthiosemicarbazone in the presence of triphenylphosphine has been achieved. The X-ray structure of the copper(I) complex **1**, showed that the geometry around copper(I) is distorted tetrahedral. The optimized geometry of the copper(I) complex displays similar coordination geometry, as the crystal structure of complex **1**.

Supplementary data

Crystallographic data for the structural analysis of complex **1** have been deposited with Cambridge Crystallographic Data Centre, under CCDC No. 1042104. Copy of this information may 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). Other supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_57A(8-9)1138-1143_SupplData.pdf.

References

1 Lobana T S, Sharma R, Bawa G & Khanna S, *Coord Chem Rev*, 253 (2009) 977.

2 Padhye S B & Kauffman G, *Coord Chem Rev*, 63 (1985) 127.

3 West D X, Padhye S B & Sonawane P B, *Struct Bonding Berlin Ger*, 76 (1991) 4.

4 West D X, Liberta A E, Padhye S B, Chikate R C, Sonawane P B, Kumbhar A S & Yerande R G, *Coord Chem Rev*, 123 (1993) 49.

5 Casas J S, Garcia-Tasende M S & Sordo J, *Coord Chem Rev*, 209 (2000) 197.

6 Smith D R, *Coord Chem Rev*, 164 (1997) 575.
7 Lobana T S, Khanna S, Sharma R, Hundal G, Sultana R, Chaudhary M, Butcher R J & Castineiras A, *Cryst Growth Design*, 8 (2008) 1203.
8 Mahajan R K, Kaur I & Lobana T S, *Talanta*, 59 (2003) 101.
9 Mahajan R K, Kaur I & Lobana T S, *Indian J Chem*, 45A (2006) 639.
10 Mahajan R K, Walia T P S, Sumanjit & Lobana T S, *Talanta*, 67 (2005) 755.
11 Sarma L S, Kumar J R, Kumar C J & Reddy A V, *Anal Lett*, 36 (2003) 605.
12 Reddy K J, Kumar J R, Ramachandraiah C, Thriveni T & Reddy A V, *Food Chem*, 101 (2007) 585.
13 Ali M A, Khalifa M E, Ghazy S E & Hassanien M M, *Anal Sci*, 18 (2002) 1235.
14 Abram U, Ortner K, Gust R & Sommer K, *J Chem Soc Dalton Trans*, (2000) 735.
15 Nomiya K, Sekino K, Ishiawa M, Honda A, Yokoyama M, Kasuga N C, Yokoyama H, Nakano S & Onodera K, *J Inorg Biochem*, 98 (2004) 601.
16 Ferrari M B, Bisceglie F, Pelosi G, Tarasconi P, Albertini R, Bonati A, Lunghi P & Pinelli S, *J Inorg Biochem*, 83 (2001) 169.
17 West D X, Ives J S, Krejci J, Salberg M M, Zumbahlen T L, Bain G A, Liberta A E, Valdes-Martinez J, Hernadez-Ortiz S & Toscano R A, *Polyhedron*, 14 (1995) 2189.
18 Garcia-Tojal J, Lezama L, Pizarro J L, Insausti M, Arriortua M I & Rojo T, *Polyhedron*, 18 (1999) 3703.
19 Lobana T S, Rekha, Butcher R J, Castineiras A, Bermejo E & Bharatam P V, *Inorg Chem*, 45 (2006) 1535.
20 Butcher R J & West D X, *Transition Met Chem*, 18 (1993) 449.
21 Lobana T S, Kumari P & Butcher R J, *Inorg Chem Commun*, 11 (2008) 11.
22 Basuli F, Ruf M, Pierpont C G & Bhattacharya S, *Inorg Chem*, 37 (1998) 6113.
23 Basuli F, Peng S M & Bhattacharya S, *Inorg Chem*, 39 (2000) 1120.
24 Ma J L, Wu J Y, Tian Y P & Zhao C Y, Chinese *J Struct Chem*, 19 (2000) 239.
25 Lobana T S, Sonia Khanna & Butcher R J, *Inorg Chem Commun*, 11 (2008) 1433.
26 Brauer G, *Handbook of Preparative Chemistry*, Vol. 2, 2nd Edn, (Academic Press, New York) 1965.
27 Sheldrick G M, *Acta Crystallogr Sect A*, 46 (1990) 467.
28 Sheldrick G M, *SHELXL-97 Program for the Refinement of Crystal Structures*, (University of Goettingen, Germany) 1997.
29 *Gaussian 09*, *Rev. A.02* (Gaussian Inc. Wallingford CT) 2009.
30 Gridnev I D, Kohrtb C & Liua Y, *Dalton Trans*, 43 (2014) 1785.
31 Lee C, Yang W & Parr R G, *Phys Rev* B, 37 (1988) 785.
32 Becke A D, *J Chem Phys*, 98 (1993) 1372.
33 Becke A D, *J Chem Phys*, 98 (1993) 5648.
34 Lobana T S, Sharma R, Castineiras A & Butcher R J, *Z Anorg Allg Chem*, 636 (2010) 2698.
35 Huheey J E, Keiter E A & Keiter R L, *Inorganic Chemistry: Principals of Structure and Reactivity*, 4th Edn, (Harper Collins College Publishers, New York) 1993.
36 Wu D H, Li Z F, Zhang Y H, *Acta Crystallogr*, E65 (2009) 163.
37 Reddy M S, Sarala Y, Jagadeesh M, Das S K & Ammireddy V R, *Acta Crystallogr*, E70 (2014) 846.
38 Hakimi M, Vahedi H, Rezvaninezhad M, Schuh E & Mohr F, *J Sulfur Chem*, 32 (2011) 55.