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Bis(triphenylphosphine)4-fluorobenzaldehyde thiosemicarbazone copper(I): Forcing chelation through oxoanions

Marisa Belicchi-Ferrari, Franco Bisceglie, Chiara Cavalieri, Giorgio Pelosi *, Pieralberto Tarasconi

Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Viale G.P. Usberti 17/A, Università degli Studi di Parma, 43100 Parma, Italy

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Abstract

This paper reports the synthesis and characterization of six compounds of copper(I), stabilized in its reduced state by two triphenylphosphines, in which 4-fluorobenzaldehyde thiosemicarbazone and *N*-methylthiosemicarbazone act as chelating through their sulfur and imino nitrogen. The three oxoanions that have been chosen, NO_3^-, SO_4^{2-} and CH_3COO^-, play an important role: their oxygens are bad competitors with the imino nitrogen of the thiosemicarbazone moiety and moreover they form strong charge assisted hydrogen bondings that stabilize the neutral form of the ligand. The overall packing is determined by intermolecular phenyl–phenyl van der Waals interactions.

Keywords: Copper(I) complexes; Thiosemicarbazones; X-ray analysis; Chelate

1. Introduction

Thiosemicarbazones are a class of very interesting compounds in many respects ranging from bonding and structural features presented by their metal complexes to their pharmacological properties [1–10]. Copper(I) complexes with various ligands with N, S, P potentially donor atoms are of interest because of their wide variation in structural motifs and rich photo-physical and chemical properties. Many of these complexes have been reported to be luminescent and their emission behaviour varies with structures and steric/electronic effects of the ligands [11–15]. The current interest on thiosemicarbazone chemistry arises also from the fact that the number of donor sites of the ligand can be modulated in order to have mono or bidentate ligands to tetradentate or polidentate macrocyclic ligands [16]. Thiosemicarbazones present a thione–thiol equilibrium that confers them a planar geometry and the two possible configurations are conventionally called *E* and *Z* with reference to the relative positions of the sulfur and the terminal hydrazinic nitrogen in the thiolic form (Scheme 1).

It is reported that in their neutral form thiosemicarbazones bind to a metal in their *E* configuration, generally via an S donor atom (Scheme 2, Ia), and after deprotonation of the hydrazinic NH hydrogen the *Z* form is preferred and they bind to the metal in an *N*,*S*-chelating mode (Scheme 2, Ib) [3,5,10,17a,17b,17c].

Here we report our studies carried out to verify if the presence of oxoanions can affect the bonding trends of this class of compounds. Despite of the wide literature reporting data relative to Cu(II) thiosemicarbazone metal complexes, few are the reports on structural considerations of complexes of thiosemicarbazones with Cu(I) [2–6,10,17]. The reason for the lack of copper(I) thiosemicarbazone studies can be related to their insolubility in many organic solvents. It has been verified that tertiary phosphines play a positive role in solubilizing Cu(I) complexes of thioamides [3] and we have therefore taken advantage from this piece of information to plan our experiments. With their d^{10}

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* Corresponding author. Tel.: +39 0521905420; fax: +39 0521905557.
E-mail address: giorgio.pelosi@unipr.it (G. Pelosi).

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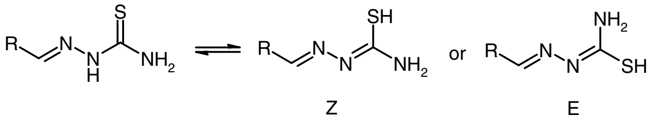
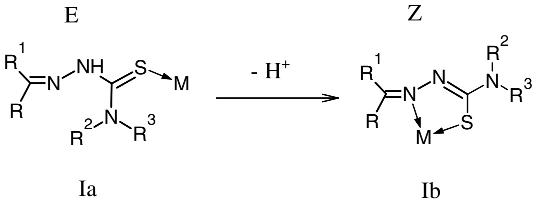
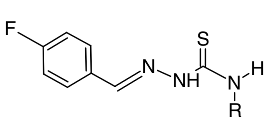


Scheme 1. Thione/thiol equilibrium and conventional nomenclature for the two thiolic forms.



Scheme 2. R^1, R^2 and R^3 can be either H or organic radicals.



Scheme 3. Chemical drawing of Hfbt ligand (R = H) and Me-Hfbt ligand ($R = CH_3$).

electronic configuration Cu(I) ions do not have an energetically preferred geometry and their coordination is therefore mainly governed by steric repulsions. Aside from the two donor species P and S the remaining space around the copper ion is usually occupied by a fourth ligand, usually a halide. In our experiments we have decided to verify if the absence of other soft species can influence the coordination and in particular if in these conditions the imino nitrogen becomes a suitable donor for coordination. In this paper, the complexes of 4-fluorobenzaldehyde thiosemicarbazones (Hfbt and Me-Hfbt, Scheme 2) with Cu(I) nitrate, sulphate and acetate in the presence of triphenylphosphine (Ph_3P) are reported. The choice of these oxoanions was envisaged to stabilize the ligand in the *Z* conformation thank to their capability to form concerted hydrogen bonds while the *N*-methylated derivative was used for comparison to verify if the terminal amino hydrogen, not involved in the aforementioned hydrogen bonds, can influence the crystal packing. All of these compounds have been characterized by elemental analysis, IR, ^{1}H NMR spectroscopy and compounds **1**, **5** and **6** also by X-ray crystallography Scheme 3.

2. Experimental

2.1. Materials and techniques

$[Cu(PPh_3)_2NO_3]$, $[Cu_2(PPh_3)_4SO_4]$ and $[Cu(PPh_3)_2(CH_3COO)]$ were prepared by reduction of the corresponding Cu(II) salt using a fourfold excess of PPh_3 in CH_3OH at reflux temperature for 1, 2 and 3 h, respectively. The white powder formed in the reaction flask was filtered to separate the product from Ph_3PO and washed first with EtOH and then with diethyl ether. $Cu(NO_3)_2 \cdot 3H_2O$, $CuSO_4 \cdot 5H_2O$, $Cu(CH_3CCO)_2 \cdot H_2O$ were procured from Carlo Erba while PPh_3 was purchased from Aldrich. C, H, N, S analyses were obtained with a Carbo-Erba 1108 instrument. IR spectra were recorded using KBr pellets on a Nicolet 5PC FTIR spectrophotometer in the 4000–400 cm^{-1} range. ^{1}H NMR spectra were recorded on a Bruker AC300 spectrometer at 300 MHz in DMSO with TMS as the internal reference.

2.2. Preparation of the ligands and of their complexes

4-Fluorobenzaldehyde thiosemicarbazone was prepared by condensation of 4-fluorobenzaldehyde with thiosemicarbazide or N^1-methylthiosemicarbazide in a 1:1 molar ratio in ethanol using the procedure reported in the literature [18].

2.2.1. Synthesis of $[Cu(PPh_3)_2(Hfbt)]NO_3$ (1)

To a stirred solution of $[Cu(PPh_3)_2NO_3]$ (1.650 g, 2.54 mmol) in methanol (30 mL) was added an equimolar amount of the ligand (0.502 g, 2.54 mmol) dissolved in methanol (30 mL). The contents were stirred for 2 h at room temperature. The clear solution was allowed to evaporate at room temperature and a yellow colored crystalline product was formed. The isolated powder was recrystallized from EtOH 95% and crystals apt for X-ray diffraction were obtained (yield: 1.400 g, 65%; m.p.: 184 °C). The complex is soluble in DMSO, $CHCl_3$ and CH_2Cl_2. *Anal.* Calc. for $C_{44}H_{38}CuFN_4O_3P_2S$: C, 62.37; H, 4.52; N, 6.61; S, 3.78. Found: C, 62.45; H, 4.17; N, 6.64; S, 3.81%. Main IR peaks (KBr, cm^{-1}): $\nu_{as}(NH_2)$ 3442 m; $\nu_s(NH_2)$ 3118 m; ν(N–H) 3284 w, $\nu(C\text{–}H_{aromatic})$ 3054 w, $\nu(C\text{–}C_{aromatic})$ 1627 s, 1506 s and 1480 s; ν(C=N) 1602 s; ν(C–P) 1433 vs; $\nu(NO_3)$ 1384 vs and 1293 s; ν(C–F) 1234 s; $\delta(C\text{–}H_{aromatic})$ 1156 m and 1093 m; ν(C=S) 827 m; $\gamma(C\text{–}H_{aromatic})$ 745 vs and 695 vs. ^{1}H NMR data (δ, ppm; DMSO-d_6): 7.25 (t, b, 8H, overlapped ligand H_m and PPh_3H_p); 7.37 (t, 12H, PPh_3H_m); 7.87 (dd, 2H, ligand H_o); 7.99 (s, 1H, C*H*=N); 8.29 and 8.39 (2 s, 1H each, NH_2); 11.61 (s, 1H, C(S)N*H*).

2.2.2. Synthesis of $[Cu(PPh_3)_2(Hfbt)]_2SO_4 \cdot CH_3OH$ (2)

To a stirred solution of $[Cu_2(PPh_3)_4SO_4]$ (0.662 g, 0.52 mmol) in methanol (20 mL) was added a twofold molar amount of the ligand (0.205 g, 1.04 mmol) dissolved in methanol (20 mL). The contents were stirred for 2 h at room temperature. A yellow powder was formed and the product was filtered (yield: 0.600 g, 68%; m.p.: 132 °C). The complex is soluble in DMSO, $CHCl_3$ and CH_2Cl_2. *Anal.* Calc. for $C_{89}H_{80}Cu_2F_2N_6O_5P_4S_3$: C, 62.93; H, 4.75; N, 4.95; S, 5.66. Found: C, 62.51; H, 4.49; N, 4.83; S, 5.50%. Main IR peaks (KBr, cm^{-1}): $\nu_{as}(NH_2)$ 3377 s; $\nu_s(NH_2)$ 3143 m; ν(N–H) 3289 m, $\nu(C\text{–}H_{aromatic})$ 3052 m, $\nu(C\text{–}C_{aromatic})$ and overlapped ν(C=N) 1602 vs, $\nu(C\text{–}C_{aromatic})$

1507 vs and 1480 s; ν(C–P) 1434 vs; ν(C–F) 1234 s; δ(C–$H_{aromatic}$) 1155 s and 1094 s; ν(SO_4) 1121 s; ν(C=S) 833 m; γ(C–$H_{aromatic}$) 745 vs and 696 vs. ^{1}H NMR data (δ, ppm; DMSO-d_6): 7.24 (t, b, 8H, overlapped ligand H_m and PPh_3H_p); 7.36 (t, 12H, PPh_3H_m); 7.45 (t, 12H, PPh_3H_o); 7.86 (bs, 2H, ligand H_o); 7.99 (s, 1H, C*H*=N); 8.29 and 8.39 (2s, 1H each, NH_2); 11.58 (s, 1H, C(S)N*H*).

2.2.3. Synthesis of [Cu(PPh_3)$_2$(Hfbt)]CH_3COO (3)

To a stirred solution of [Cu(PPh_3)$_2$(CH_3COO)] (0.672 g, 1.04 mmol) in methanol (25 mL) was added an equimolar amount of the ligand (0.205 g, 1.04 mmol) dissolved in methanol (25 mL). The contents were stirred for 2 h at room temperature. The clear solution was allowed to evaporate and a yellow product was afforded (yield: 0.650 g, 76%; dec.: 178 °C). The complex is soluble in DMSO, $CHCl_3$ and CH_2Cl_2. *Anal.* Calc. for $C_{46}H_{41}CuFN_3O_2P_2S$: C, 65.43; H, 4.89; N, 4.98; S, 3.80. Found: C, 65.84; H, 4.78; N, 5.01; S, 3.69%. Main IR peaks (KBr, cm^{-1}): ν(NH_2) 3481 m, 3382 m, 3141 w; ν(NH) 3293 m, 3238 w; ν(C–$H_{aromatic}$) 3052 m; ν_{as}(COO) 1580 s; ν(C–$C_{aromatic}$) 1596 s and 1478 s; ν(C–P) 1434 vs; ν(C–F) 1229 s; δ(C–$H_{aromatic}$) 1156 m and 1094 m; ν(C=S) 834 m; γ(C–$H_{aromatic}$) 746 vs and 696 vs. ^{1}H NMR data (δ, ppm; DMSO-d_6): 2.10 (bs, 3H, CH_3COO); 7.26 (t, b, 8H, overlapped ligand H_m and PPh_3H_p); 7.40 (t, 12H, PPh_3H_m); 7.52 (t, 12H PPh_3H_o); 7.95 (dd, 2 H, ligand H_o); 8.06 (s, 1H, C*H*=N); 8.30 and 8.41 (2s, 1H each, NH_2); 11.54 (s, 1H, C(S)N*H*).

2.2.4. Synthesis of [Cu(PPh_3)$_2$(Me-Hfbt)]NO_3 · CH_3OH (4)

To a stirred solution of [Cu(PPh_3)$_2$$NO_3$] (1.134 g, 1.75 mmol) in methanol (25 mL) was added an equimolar amount of the ligand (0.368 g, 1.74 mmol) dissolved in methanol (20 mL). The contents were stirred for 2 h at room temperature. The clear solution was allowed to evaporate at room temperature and a yellow colored powder was obtained (yield: 1.078 g, 69%; m.p.: 100 °C). The complex is soluble in DMSO, $CHCl_3$ and CH_2Cl_2. *Anal.* Calc. for $C_{46}H_{44}CuFN_4O_4P_2S$: C, 61.84; H, 4.96; N, 6.27; S, 3.59. Found: C, 61.72; H, 4.65; N, 6.31; S, 3.53%. Main IR peaks (KBr, cm^{-1}): ν(N–H) 3382 m, 3239 m, ν(C–$H_{aromatic}$) 3052 w; ν(C–$H_{aliphatic}$) 2998 m; ν(C–$C_{aromatic}$) 1601 s, 1507 s and 1480 s; ν(C=N) 1566 s; ν(C–P) 1434 vs; ν(NO_3) 1384 vs and 1292 s; ν(C–F) 1234 s; δ(C–$H_{aromatic}$) 1156 m and 1093 m; ν(C=S) 834 w; γ(C–$H_{aromatic}$) 746 vs and 696 vs. ^{1}H NMR data (δ, ppm; DMSO-d_6): 2.99 (d, 3H, NCH_3); 7.24 (t, b, 8H, overlapped ligand H_m and PPh_3 H_p); 7.37 (t, 12H, PPh_3H_m); 7.47 (t, 12H PPh_3H_o); 7.86 (dd, 2H, ligand H_o); 7.99 (s, 1H, C*H*=N); 8.56 (s, 1H, N*H*CH_3); 11.44 (s, 1H, C(S)N*H*).

2.2.5. Synthesis of [Cu(PPh_3)$_2$(Me-Hfbt)]$_2$$SO_4$ (5)

To a stirred solution of [Cu_2(PPh_3)$_4$$SO_4$], (0.631 g, 0.50 mmol) in methanol (35 mL) was added a twofold molar amount of the ligand (0.209 g, 1.00 mmol) dissolved in methanol (15 mL). The contents were stirred for 2 h at room temperature. The clear solution was allowed to evaporate at room temperature and a yellow colored crystalline product was formed. The isolated powder was dissolved in warm EtOH 95% and crystals apt for X-ray diffraction were obtained (yield: 1.050 g, 62%; m.p.: 143 °C). The complex is soluble in DMSO, $CHCl_3$ and CH_2Cl_2. *Anal.* Calc. for $C_{90}H_{80}Cu_2F_2N_6O_4P_4S_3$: C, 63.78; H, 4.76; N, 4.96; S, 5.68. Found: C, 63.55; H, 4.68; N, 4.91; S, 5.51%. Main IR peaks (KBr, cm^{-1}): ν(NH) 3446 w, 3378 w, 3226 w; ν(C–$H_{aromatic}$) 3051 m; ν(C–$H_{aliphatic}$) 2934 m; ν(C–$C_{aromatic}$) 1602 s, 1508 vs and 1480 s; ν(C=N) 1567 m; ν(C–P) 1435 vs; ν(C–N) 1329 m; ν(C–F) 1233 s; δ(C–$H_{aromatic}$) 1156 m and 1093 m; ν(SO_4) 1118 s; ν(C=S) 831 m; γ(C–$H_{aromatic}$) 746 vs and 697 vs. ^{1}H NMR data (δ, ppm; DMSO-d_6): 2.08 (s, 3H, NCH_3); 7.25 (t, b, 8H, overlapped ligand H_m and PPh_3 H_p); 7.37 (t, 12H, PPh_3H_m); 7.44 (t, 12H PPh_3H_o); 7.86 (dd, 2H, ligand H_o); 8.00 (s, 1H, C*H*=N); 8.27 (s, 1H, N*H*CH_3); 11.54 (s, 1H, C(S)N*H*).

2.2.6. Synthesis of {[Cu(PPh_3)$_2$(Me-Hfbt)] CH_3COO}$_2$ · 2EtOH · H_2O (6)

To a stirred solution of [Cu(PPh_3)$_2$(CH_3COO)] (0.619 g, 0.96 mmol) in ethanol 95% (25 mL) was added an equimolar amount of the ligand (0.202 g, 0.96 mmol) dissolved in ethanol (15 mL). The contents were stirred for 2 h at reflux temperature. The clear solution was allowed to evaporate at room temperature and yellow-brown crystals suitable for X-ray diffraction were afforded (yield: 1.280 g, 74%; m.p.: 144 °C). The complex is soluble in DMSO, $CHCl_3$ and CH_2Cl_2. *Anal.* Calc. for $C_{98}H_{100}Cu_2F_2N_6O_7P_4S_2$: C, 64.42; H, 5.52; N, 4.60; S, 3.51. Found: C, 64.45; H, 5.55; N, 4.62; S, 3.53%. Main IR peaks (KBr, cm^{-1}): ν(NH) 3378 w, 3238 w; ν(C–$H_{aromatic}$) 3053 m; ν(C–$H_{aliphatic}$) 2970 m; ν_{as}(COO) 1619 vs; ν_s(COO) 1396 s; ν(C–$C_{aromatic}$) 1599 vs, 1507 vs and 1480 vs; ν(C–P) 1434 vs; ν(C–F) 1232 s; δ(C–$H_{aromatic}$) 1156 m and 1093 m; ν(C=S) 832 m; γ(C–$H_{aromatic}$) 746 vs and 697 vs. ^{1}H NMR data (δ, ppm; DMSO-d_6): 1.18 (t, 3H, C$H_3$$CH_2$OH), 2.10 (bs, 6H, NC$H_3$ + CH_3COO); 3.72 (q, 2H, CH_3CH_2OH), 7.28 (t, b, 8H, overlapped ligand H_m and PPh_3 H_p); 7.39 (t, 12H, PPh_3H_m); 7.48 (t, 12H PPh_3H_o); 7.91 (dd, 2H, ligand H_o); 8.04 (s, 1H, C*H*=N); 8.34 (s, 1H, N*H*CH_3); 11.58 (s, 1H, C(S)N*H*).

2.3. Crystallography

Relevant data concerning data collection and details of structure refinement are summarized in Table 1. Intensity data were collected on a Philips PW1100 (compounds **1** and **6**) and on a SMART 1000 Bruker AXS diffractometer (compound **5**) with Mo Kα radiation. Data from crystals of compounds **1** and **6** collected on the Philips diffractometer were non corrected for absorption while for compound **5** an absorption correction was carried out using the SADABS [19] procedure. The WINGX [20] package was used all through the refinement and completion of the structure. The structures were solved using direct methods (SIR-97 [21]). Refinements were carried out by full matrix least-

Table 1
Experimental data for crystallographic analyses

Compound	**1**	**2**	**3**
Chemical formula	$C_{44}H_{38}CuFN_4O_3P_2S$	$C_{90}H_{80}Cu_2F_2N_6O_4P_4S_3$	$C_{98}H_{100}Cu_2F_2N_6O_7P_4S_2$
Formula weight	847.32	1694.74	1827.01
Space group (no.)	$P\bar{1}(2)$	$P2_1/c(14)$	$P\bar{1}(2)$
a (Å)	13.490(3)	18.117(3)	14.168(1)
b (Å)	14.064(3)	18.336(3)	17.550(1)
c (Å)	11.318(3)	25.211(4)	20.231(1)
α (°)	94.36(2)	90.0	108.638(1)
β (°)	106.47(3)	91.830(3)	94.385(1)
γ (°)	96.37(2)	90.0	90.019(1)
V (Å^3)	2033.4(9)	8371(2)	4751.0(5)
Z	2	4	2
F(000)	876	3512	1908
T (K)	298.15	298.15	298.15
D_{calc} (Mg/m^3)	1.384	1.345	1.277
μ (cm^{-1})	7.17	7.18	6.19
λ (Å)	0.71069	0.71069	0.71069
R	0.056	0.0548	0.0486
Rw_2	0.1021	0.1184	0.0992

$R = \sum||F_o|| - F_c||/\sum|F_o|$.
$Rw_2 = \left\{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\right\}^{1/2}$.

squares cycles SHELXL97 [22] for all compounds. The hydrogen atoms were calculated with standard geometry and refined in riding position. Atomic scattering factors were taken from the International Tables for Crystallography [23]. The program PARST [24] was employed for the geometrical description and ORTEP [25] and MERCURY [26] for the drawings.

3. Results and discussion

3.1. Synthesis and spectroscopy

Compounds (**1**), (**5**) and (**6**) afforded crystals suitable for X-ray diffraction studies and structural data allow for a correlation between structures and spectroscopic data. As for complexes obtained from NO_3^- is concerned, the IR spectral behaviour of (**1**) and (**4**) is very similar in all the observed range. This allows to suppose that the Me-Hfbt ligand of complex (**4**) is in the same environment of complex (**1**). It is useful to note that the same differences found between complex (**1**) and its free ligand are also found between (**4**) and its free ligand. The IR absorptions of the C=S groups are shifted at lower frequencies with respect to the free ligand (827 cm^{-1} for (**1**) versus 836 cm^{-1} and 834 cm^{-1} for (**4**) versus 837) indicating the weakening of the C=S bond after coordination. Changes in the spectral ranges between 1500 and 1600 cm^{-1} (νC=N) and between 1130 and 1340 cm^{-1} (NC(=S)N absorptions) indicate the C=N involvement in coordination. It can also be generally observed a broadening of the ν(NH) absorptions, showing a different behaviour of the hydrogen bonding network in the complexes with respect to the free ligands. This can be due to the fact that also in the free ligands at the solid state N–H bonds are involved in strong hydrogen bonds. For this reason it is not always observed in the IR spectra of complexes a shift to lower frequencies with respect to the free ligand. The absorption at *ca.* 1394 and 1293 cm^{-1} are assigned to the absorptions of the non coordinated inorganic ligand. NMR data suggest that also in solution ligands are in their neutral form as can be observed from the presence at 11.61 ppm for (**1**) and 11.44 ppm for (**4**). With respect of NMR data of the free ligands, a slight shift to low field of N–H protons is observed (up to 0.20 ppm).

Similar considerations can be also drawn for complexes (**2**) and (**5**) obtained from SO_4^{2-} and (**3**) and (**6**) from CH_3COO^- anions. In particular for (**2**) and (**5**) can be observed the presence at 1120 cm^{-1} strong absorption of ionic SO_4^{2-}. The IR spectra of complexes (**3**) and (**6**) result more complicated because of the presence of CH_3COO^- asymmetric and symmetric stretchings.

In this way for all complexes a tetrahedral coordination by means of S,N, P, P can be assumed.

3.2. Crystal structures of the complexes

The syntheses allowed to isolate in crystalline form complexes (**1**), (**5**) and (**6**) and in order to establish their structural features, single crystal X-ray crystallography experiments were carried out (Table 2).

In Fig. 1 is reported the ORTEP view of complex $Cu(PPh_3)_2(Hfbt)]NO_3$ (**1**). The structure can be described as formed by a cationic complex molecule with a nitrate as a counterion and the copper(I) ion coordinates two triphenylphosphines and a parafluorobenzaldehyde thiosemicarbazone molecule in its neutral form. The thiosemicarbazone binds to the metal through the sulfur and the iminic nitrogen and forms a five-term chelation ring with an angle N–Cu–S of 85.13(5)°. The P–Cu–P angle is rather

Table 2
Selected bond distances (Å) and angles (°) for compounds **1**, **5** and **6**

	1	**5**		**6**	
Cu(1)–P(1)	2.3056(7)	2.273(2)	2.261(2)	2.294(1)	2.284(1)
Cu(1)–P(2)	2.2521(7)	2.295(2)	2.286(2)	2.293(1)	2.260(1)
Cu(1)–S(1)	2.3482(8)	2.354(2)	2.337(3)	2.337(1)	2.338(1)
Cu(1)–N(3)	2.136(2)	2.164(6)	2.117(8)	2.162(4)	2.171(4)
N(2)–N(3)	1.380(2)	1.387(8)	1.350(9)	1.386(5)	1.376(5)
C(1)–N(1)	1.327(3)	1.338(9)	1.331(10)	1.330(6)	1.329(5)
C(1)–N(2)	1.337(3)	1.341(9)	1.331(12)	1.349(6)	1.345(5)
C(1)–S(1)	1.693(2)	1.685(8)	1.709(9)	1.688(5)	1.689(4)
C(2)–N(3)	1.286(2)	1.290(9)	1.323(10)	1.282(5)	1.293(5)
C(2)–C(3)	1.454(3)	1.457(11)	1.425(12)	1.462(6)	1.453(7)
C(3)–C(8)	1.381(3)	1.374(11)	1.363(13)	1.385(6)	1.372(7)
C(3)–C(4)	1.380(3)	1.352(11)	1.425(13)	1.388(6)	1.395(7)
C(4)–C(5)	1.374(3)	1.374(12)	1.419(14)	1.376(7)	1.374(9)
C(5)–C(6)	1.356(3)	1.318(13)	1.355(15)	1.362(7)	1.345(10)
C(6)–F(1)	1.352(3)	1.382(10)	1.370(13)	1.362(6)	1.359(7)
C(6)–C(7)	1.357(4)	1.336(13)	1.324(17)	1.363(7)	1.363(9)
C(7)–C(8)	1.375(4)	1.385(12)	1.380(16)	1.380(6)	1.374(7)
C(9)–N(1)		1.440(10)	1.444(11)	1.441(6)	1.444(6)
N(3)–Cu(1)–P(2)	125.07(5)	102.6(2)	114.8(2)	113.9(1)	122.8(1)
N(3)–Cu(1)–P(1)	99.64(5)	114.9(2)	108.1(2)	116.3(1)	104.1(1)
P(2)–Cu(1)–P(1)	126.83(3)	135.39(8)	128.52(9)	121.20(5)	123.15(5)
N(3)–Cu(1)–S(1)	85.13(5)	83.9(2)	85.8(2)	84.8(1)	83.8(1)
P(2)–Cu(1)–S(1)	110.68(3)	104.65(8)	107.46(9)	108.15(5)	106.55(5)
P(1)–Cu(1)–S(1)	99.21(3)	102.69(8)	102.65(9)	104.93(5)	108.88(5)
C(1)–N(1)–C(9)		122.3(7)	123.5(9)	124.7(5)	124.3(4)
C(1)–N(2)–N(3)	122.8(2)	121.1(6)	123.1(8)	122.7(4)	123.0(4)
C(2)–N(3)–N(2)	112.9(2)	113.7(6)	113.0(8)	113.8(4)	114.1(4)
C(2)–N(3)–Cu(1)	133.5(1)	132.8(5)	134.3(6)	134.4(3)	131.4(3)
N(2)–N(3)–Cu(1)	111.6(1)	112.9(5)	112.6(6)	111.8(3)	111.4(3)
N(1)–C(1)–N(2)	115.1(2)	113.1(7)	116.0(9)	114.4(4)	115.0(4)
N(1)–C(1)–S(1)	121.1(2)	123.1(7)	120.8(8)	122.4(4)	122.7(4)
N(2)–C(1)–S(1)	123.7(2)	123.7(6)	123.2(7)	123.1(4)	122.3(4)
N(3)–C(2)–C(3)	125.4(2)	122.4(8)	124.5(9)	126.1(4)	124.8(5)
C(8)–C(3)–C(4)	117.7(2)	117.5(8)	116.9(10)	118.0(5)	118.4(5)
C(8)–C(3)–C(2)	117.7(2)	119.9(8)	116.2(11)	123.9(4)	123.8(5)
C(4)–C(3)–C(2)	124.6(2)	122.6(8)	126.6(10)	118.1(4)	117.8(5)
C(5)–C(4)–C(3)	121.8(2)	122.3(9)	121.8(10)	121.1(5)	119.9(6)
C(6)–C(5)–C(4)	118.3(2)	118.1(10)	116.8(12)	118.8(5)	119.5(6)
F(1)–C(6)–C(5)	119.1(2)	119.0(11)	115.7(13)	119.4(5)	119.1(7)
F(1)–C(6)–C(7)	118.6(2)	117.7(10)	119.6(13)	118.2(5)	118.3(8)
C(5)–C(6)–C(7)	122.2(2)	123.2(9)	124.6(13)	122.4(5)	122.6(6)
C(6)–C(7)–C(8)	118.9(3)	118.5(9)	118.7(13)	118.4(5)	118.0(6)
C(7)–C(8)–C(3)	121.0(3)	120.3(9)	121.0(12)	121.4(5)	121.6(5)

wide (125.07(5)°) and the copper tetrahedral coordination is therefore strongly distorted. The coordination bonds have distances that range from 2.136(2) Å for the Cu1–N3 bond to 2.3482(8) Å for the Cu1–S1 bond. The nitrate ion forms a strong charge assisted H-bonding with the thiosemicarbazone NH groups through two of its oxygens (see Table 3). The thiosemicarbazone moiety, that should be expected to be planar because of the extended conjugated system of double bonds, is significantly distorted: the angle between the average plane of the 4-fluorobenzaldehyde ring and that of the thiosemicarbazide moiety is 23.63(7)°. This distortion can be interpreted as a double interaction of the fluorophenyl moiety with two phenyls belonging to two different triphenylphosphines.

The main feature that characterizes the packing of these molecules is a so-called sixfold phenyl embrace (6PE) [27a,27b,27c,27d] (P1…P1^{I} $I = (1 - x, -y, -z)$ distance 6.979 Å) (see Fig. 2) between two centrosymmetrically related molecules. The phenyls of the triphenylphosphines involved in this interaction present what the aforementioned paper calls a "good rotor" conformation with torsion angles (defined by the copper, the phosphorus, the ipso carbon and the next carbon atom of the phenyl group which gives the torsion angle in the range 90°, −90°) of 43.53°, 45.69° and 49.21° while the other triphenylphosphine has a more irregular conformation (torsion angles of 23.90°, 37.31°, 78.23°) due to an edge-to-face interaction between the fluorobenzene group with a tpp phenyl group.

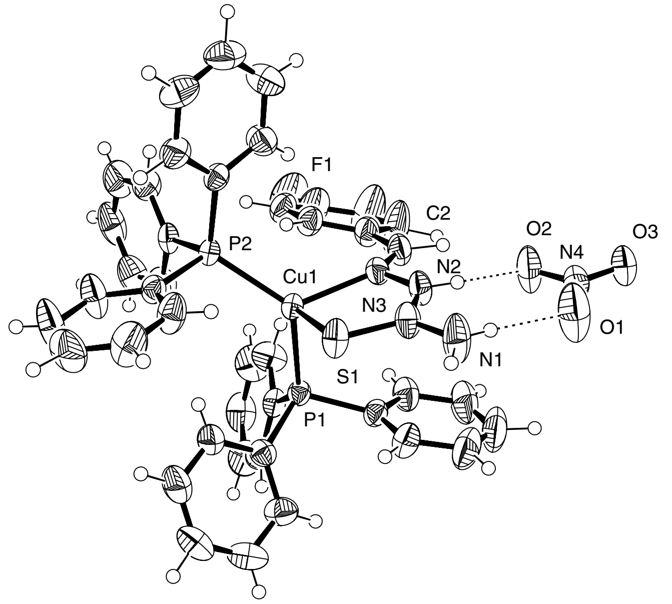


Fig. 1. ORTEP drawing of complex Cu(PPh$_3$)$_2$(Hfbt)]NO$_3$ (**1**) showing thermal ellipsoids at the 50% probability level.

Table 3
Relevant hydrogen bonds (Å, °) found in molecule **1**, **5** and **6**

Compound **1**	N1…O1(nitrate)	2.906(3)	N1–H…O1	178(3)
	N2…O2(nitrate)	2.717(2)	N2–H…O2	166(3)
Compound **5**	N1…O4(sulfate)	2.751(9)	N1–H…O4	135.5(5)
	N2…O3(sulfate)	2.740(9)	N2–H…O3	156.4(5)
	N4…O2(sulfate)	2.757(10)	N4–H…O2	153.4(5)
	N5…O1(sulfate)	2.902(10)	N5–H…O1	170.2(5)
Compound **6**	N1…O2(acetate 1)	2.701(7)	N1–H…O2	168.6(3)
	N2…O1(acetate 1)	2.746(6)	N2–H…O1	160.1(3)
	N4…O4(acetate 2)	2.805(6)	N4–H…O4	165.4(3)
	N5…O3(acetate 2)	2.720(6)	N5–H…O3	168.6(3)
	O5(ethanol)…O1 (acetate)	2.645(6)	O5–H…O1	145.4(4)
	O6(ethanol)…O4 (acetate)	2.792(9)	O6–H…O4	154.6(6)

To complete the description of the packing it is noteworthy to observe the presence of two longer P…P distances due to the presence of two pairs of phenyls belonging to two centrosymmetrically related molecules that interact edge-to-face (see Fig. 2). The other N terminal hydrogen atom seem to play no role in the packing.

The structure of compound **5**, [Cu(PPh$_3$)$_2$(Me-Hfbt)]$_2$SO$_4$, is reported in Fig. 3. The asymmetric unit is formed by two complex [Cu(PPh$_3$)$_2$(Me-Hfbt)]$^+$ cations bridged by a sulfate anion. The two cationic moieties differ significantly in their geometrical features. One of the thiosemicarbazone ligand (molecule A) presents a marked dihedral angle (43.6(3)°) between the average plane of the thiosemicarbazide moiety and that of the fluorobenzyl ring, while in the other (molecule B) is almost planar (the same dihedral angle is 2.91(3)°). The sulfate ion forms two charge assisted H-bonds connecting the two complex molecules A and B (see Table 3).

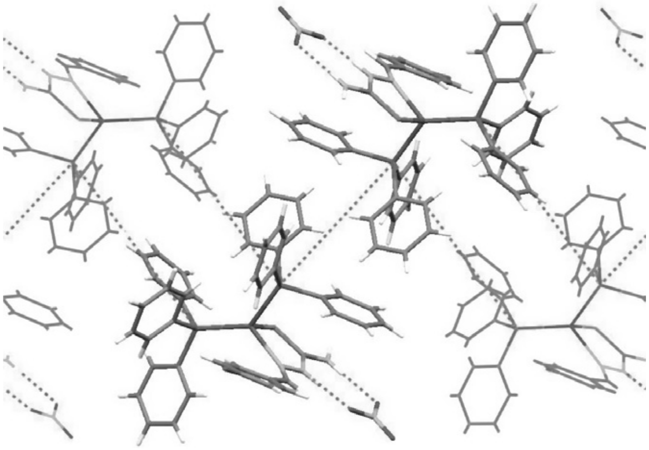


Fig. 2. MERCURY drawing of the packing of compound (**1**) showing the two molecules (capped sticks) involved in the six phenyl embrace and the looser pheny–phenyl interactions between adjacent molecules (in wireframe).

Also this packing is determined by a very tight six-atom phenyl embrace characterized by a P4…P4^I ($I = -x, 1-x, -z$) interaction with a distance of 6.645 Å (see Fig. 4), much shorter than that observed in the previous one. A looser sixfold phenyl embrace is observed between P2 and P3^I ($I = -x, -1/2+y, 1/2-z$) (distance 7.66 Å) and this interaction together with the previously described contact form a bidimensional layer of molecules that lie on the *yz* plane. These layers are connected by a third interaction between two tpp that is characterized by a longer P…P distance of 7.785 Å [P1…P3^I $I = 1+x, y, z$].

The crystal structure of compound **6** {[Cu(PPh$_3$)$_2$(Me-Hfbt)]CH$_3$COO}$_2 \cdot 2$EtOH $\cdot$ H$_2$O is reported in Fig. 5. In the asymmetric unit are present two independent complex cations, two acetate ions, two ethanol molecules and a water. The carboxyl group of the acetate forms two hydrogen bonds (see Table 3) with the NH groups of the thiosemicarbazide moiety in a way analogous to that observed in the nitrate derivative previously discussed (**1**). Moreover one of the two carboxylic oxygens (different in molecule A and in molecule B, see Fig. 6) in both acetates is also involved in a bifurcated but strong hydrogen bond with the ethanols (see Table 3). As in the previous case in the two complex molecules the thiosemicarbazone ligands have different planarities and precisely a dihedral angle between the thiourea moiety and the aromatic ring of 8.5(2)° in molecule A and 37.0(2)° in molecule B. Noteworthy the P–Cu–P angles [121.20(5)° and 123.15(5)°] that are by far smaller than those found in the other two complexes [126.83(3)° in compound **1** and 135.39(8)° and 128.52(9)° in compound **5**].

A series of considerations must be done on the hydrogen bonding system found in these compounds. A common feature is the strong charge assisted hydrogen bondings that stabilize the ligand in its neutral form. In particular some

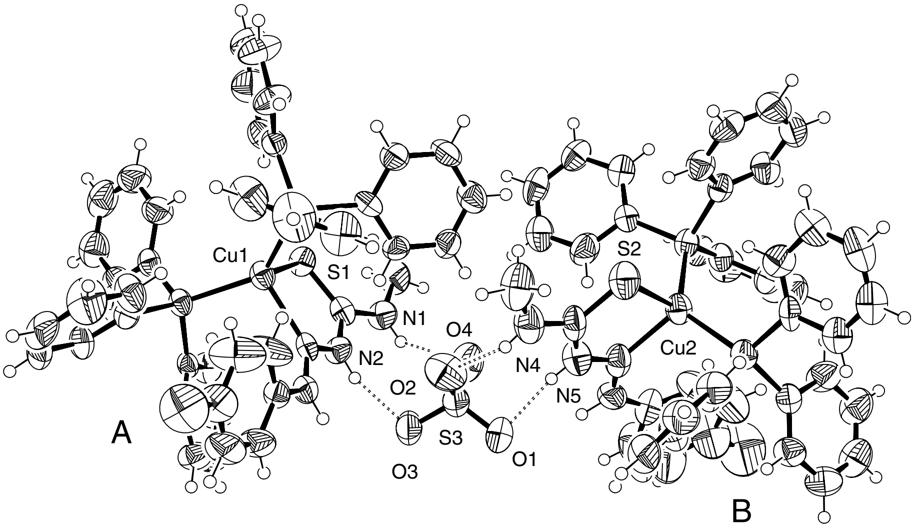


Fig. 3. ORTEP drawing of complex $[Cu(PPh_3)_2(Me\text{-}Hfbt)]_2SO_4$ (**5**) showing thermal ellipsoids at the 50% probability level.

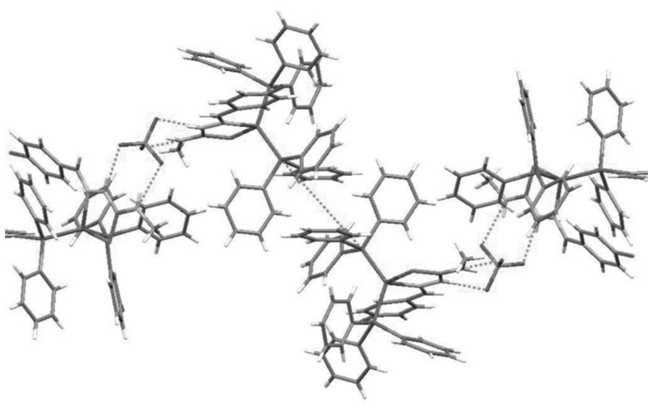


Fig. 4. MERCURY drawing of the packing of compound (**5**) showing two sulphate bridged dimeric molecules involved in the P4…P4 six phenyl embrace.

of these hydrogen bonds formed with the acidic hydrazinic nitrogen are among the shortest observed in the literature. Using a thiourea moiety as a reference we have found in the CSD [28a,28b] that the average N–H…O distance is 2.918(8) Å for the nitrate ion, 2.872(12) Å for the sulfate ion and 2.882(9) Å for the acetate that are comparable with the distances observed for the aminic NH in compound **1** (2.906(3) Å) while those found in complex **5** (2.751(33) and 2.757(10) Å) and in compound **6** (2.701(7) and 2.805(6) Å) are remarkably shorter. The hydrogen bonds that involve the hydrazinic nitrogen are very strong with distances of 2.717(2) Å for **1**, 2.740(9) Å in **5** and 2.746(6) Å and 2.720(6) Å in **6**. The only exception is the hydrazinic N of molecule B of compound **5** (2.902(9) Å) in which the distance is larger than the average and this distortion is probably due to the packing.

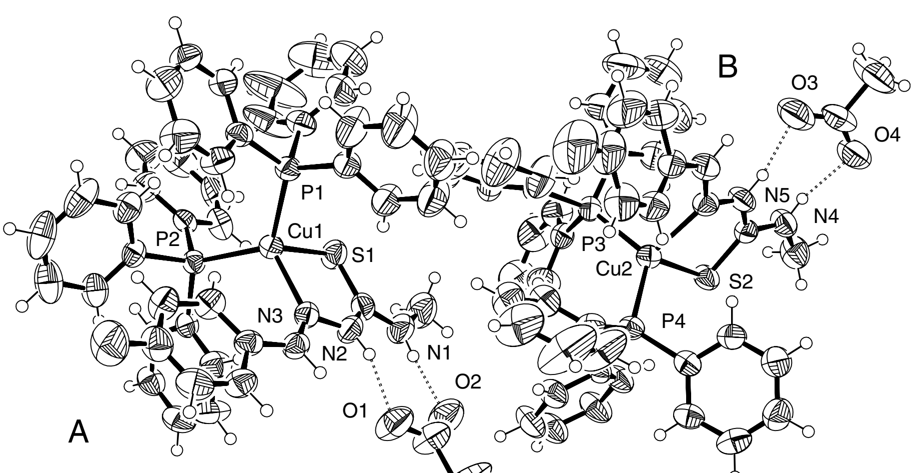


Fig. 5. ORTEP drawing of the moiety $\{[Cu(PPh_3)_2(Me\text{-}Hfbt)]CH_3COO\}_2$ of complex (**6**) showing thermal ellipsoids at the 50% probability level.

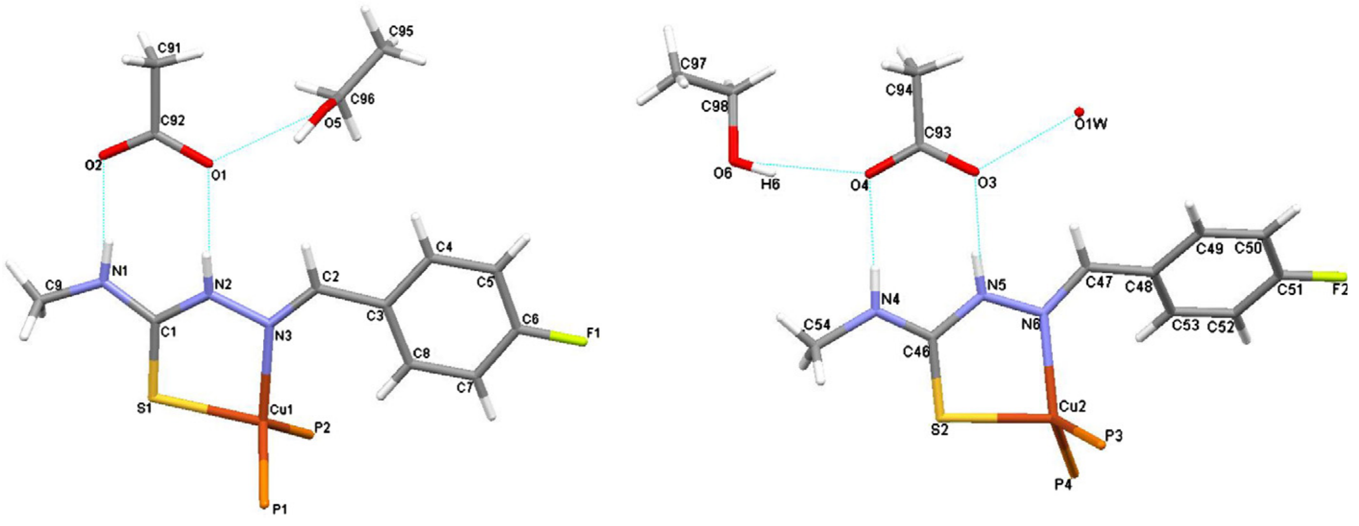


Fig. 6. MERCURY drawings of the hydrogen bond patterns around the acetate ion in the two independent molecules in compound **6**.

4. Conclusions

As hypothesized in the introduction the main features presented by these copper(I) complex molecules are determined by three factors: (a) the absence of soft donor atoms, besides P and S, that force the imino nitrogen to coordinate to the metal center; (b) the overall flatness of the thiosemicabazone moiety that allows its insertion in the cleft formed by the bulky blob of the two triphenylphosphines and, (c) the presence of the charged assisted hydrogen bonds formed by the anions that contribute to the *Z* configuration of the ligand. A contribution that is not predictable in the detail but that is decisive in understanding the overall packing and some distortions in the planarity of the thiosemicarbazone ligand in the crystal is the extended system of weak interactions among the aromatic rings.

Appendix A. Supplementary material

CCDC 640078, 640079 and 640080 contain the supplementary crystallographic data for **1**, **5** and **6**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.04.026.

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