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Synthesis, characterization and crystal structure of triphenylphosphine copper(I) methylpyruvate thiosemicarbazones

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ABSTRACT

This paper reports the synthesis of a series of methylpyruvate thiosemicarbazone derivatives containing, on the terminal nitrogen, substituents of different nature and size and namely, ethyl, phenyl and methylphenyl. These ligands were reacted with bis(triphenylphosphine)copper(I) nitrate and acetate to produce the respective complexes: $[Cu(PPh_3)_2(Et\text{-}Hmpt)]_2(NO_3)_2$ (**1**), $[Cu(PPh_3)_2(Ph\text{-}Hmpt)]NO_3$ (**2**), $[Cu(PPh_3)_2(MePh\text{-}Hmpt)]NO_3$ (**3**), $[Cu_2(O_2CCH_3)(Et\text{-}pt)(PPh_3)_2] \cdot H_2O$ (**4**), $[Cu(Ph\text{-}mpt)(PPh_3)]$ (**5**) and $[Cu_2(MePh\text{-}mpt)_2(PPh_3)_2]$ (**6**). All of them were characterized by elemental analysis, IR, ^1H NMR, EPR spectroscopy and, for compounds **1**, **2**, **4**, and **6**, by X-ray crystallography. The characterization revealed that the coordinating behaviour of the ligands is influenced by a series of factors, predominant among which is the hard soft nature of the atoms involved in the interactions with the metal centre. The complexes obtained from the nitrate copper(I) salt are formed by cationic molecules with a nitrate as a counterion, while those derived from the acetate salt present deprotonated ligands and a few unexpected features. In particular, one of the compounds (**4**) is a mixed valence dinuclear complex with an acetate oxygen and the thiosemicarbazone sulfur acting as bridging between the two Cu(I) and Cu(II) ions. Another one (**6**) presents instead a Cu(I)–Cu(I) sulfur bridged binuclear cluster.

1. Introduction

Thiosemicarbazones are being extensively studied for their biological and chemical properties. The former give them interesting pharmacological properties (antiviral, antibacterial or antitumoral activities) and the amount of recent literature concerning this subject is steadily increasing [1–10]. The chemical properties are, on the other hand, more wanting, even though the nature of thiosemicarbazones as polydentate ligands makes them very versatile molecules. In spite of the wide literature reporting data concerning copper(II) complexes with thiosemicarbazones, reports containing structural considerations about copper(I) complexes are more limited [2–6,10,11–22].

Our research group has been working on the biological activity of these compounds and recently we have started a research programme aimed at understanding how the oxidation state of copper influences the biological activity of these compounds. In this framework, our attention is presently devoted to the synthesis of copper(I) thiosemicarbazones and to their stabilization in aqueous solution. We have started our experiments from bis(triphenylphosphine)copper(I) salts, namely from the nitrate and the acetate, for two reasons: first, triphenylphosphine (tpp) is known to stabilize copper in its lower oxidation state and, second, tertiary phosphines are reported to enhance the solubility of Cu(I) thioamide complexes, that otherwise would be insoluble in many organic solvents [3].

In the literature it is reported that, in their neutral form, bidentate thiosemicarbazones bind to a metal in their *E* configuration, generally via the S donor atom (Scheme 1, Ia), while if the hydrazinic NH hydrogen is deprotonated they generally change into the *Z* form and bind to the metal in N,S-chelating mode (Scheme 1, Ib) [3,5,10,11–22]. Recently we have noticed that, more than the deprotonation, it is the nature of the ligand and the presence or absence of soft ligand competitors that influence the coordination mode of these ligands [23].

In fact, acting on the solvent and on the copper salt counterions, we have managed to impose a chelating behaviour (*Z* configuration) to the reported ligands even though these were protonated.

In this paper we report our studies concerning the use of a potentially terdentate S,N,O ligand, namely methylpyruvate thiosemicarbazone [Hmpt], and the influence of the thiosemicarbazide terminal nitrogen substituents on the coordination behaviour and the stability of these compounds. To this scope we used a series of previously synthesized derivatives of methylpyruvate thiosemicarbazone containing, on the terminal nitrogen, substituents of different nature and size: ethyl, phenyl and methylphenyl (Scheme 2) [24].

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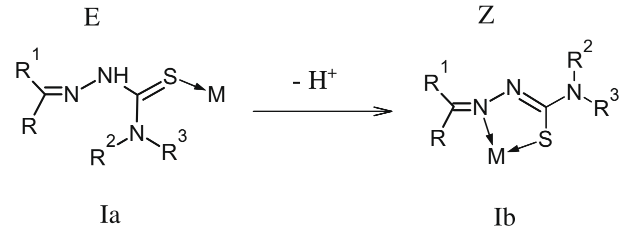
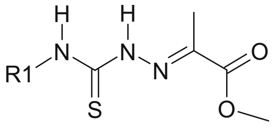


Scheme 1. R^1, R^2 and R^3 can be either H or organic radicals.



Scheme 2. Chemical drawing of Hmpt ligand (R1 = ethyl, phenyl and 3-methylphenyl).

These ligands were then reacted with bis(triphenylphosphine)copper (I) nitrate and acetate and the complexes so obtained, $[Cu(PPh_3)_2(Et\text{-}Hmpt)]_2(NO_3)_2$ **1**, $[Cu(PPh_3)_2(Ph\text{-}Hmpt)]NO_3$ **2**, $[Cu(PPh_3)_2(MePh\text{-}Hmpt)]NO_3$ **3**, $[Cu_2(O_2CCH_3)(Et\text{-}pt)(PPh_3)_2] \cdot H_2O$ **4**, $[Cu(Ph\text{-}mpt)(PPh_3)]$ **5** and $[Cu_2(MePh\text{-}mpt)_2(PPh_3)_2]$ **6**, are reported here. All of them have been characterized by elemental analysis, IR, ^1H NMR spectroscopy and compounds **1**, **2**, **4**, and **6** also by X-ray crystallography. Compound **4** contains two copper atoms with two totally different geometries suggesting, together with the charge balance, the presence of two different oxidation states. For this compound also an EPR spectroscopy analysis was carried out.

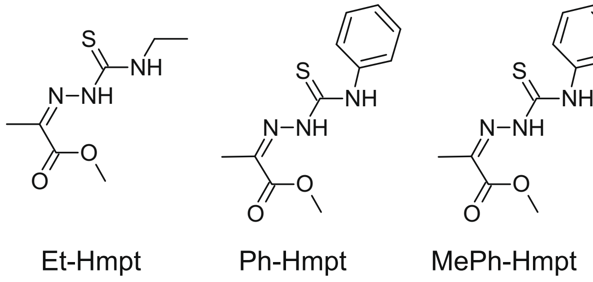
2. Experimental

2.1. Materials and techniques

$[Cu(PPh_3)_2NO_3]$ 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 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. $Cu(NO_3)_2 \cdot 3H_2O$ and $Cu(CH_3COO)_2 \cdot H_2O$ were procured from Carlo-Erba, while PPh_3 was purchased from Aldrich. C, H, N, S analyses were obtained with a Carlo-Erba 1108 instrument. IR spectra were recorded using KBr pellets on a Nicolet 5PC FT-IR spectrophotometer in the 4000–400 cm^{-1} range. ^1H NMR spectra were recorded on a Bruker AC300 spectrometer at 300 MHz in d_6–DMSO with TMS as the internal reference. EPR spectra, both at room and liquid nitrogen temperature, were recorded in phase-sensitive detection by a X-band (9-GHz) Varian V-4502 spectrometer with a 100 kHz field modulation.

2.2. Preparation of the ligands

Methylpyruvate thiosemicarbazones were prepared by condensation of methylpyruvate with N^1-substituted thiosemicarbazides in a 1:1 molar ratio in methanol using the procedure reported in the literature [24]. In this way methylpyruvate-N^1-ethylthiosemicarbazone (Et-Hmpt · H_2O, used to prepare complexes **1** and **4**), methylpyruvate-N^1-phenylthiosemicarbazone (Ph-Hmpt, used to prepare complexes **2** and **5**) and methylpyruvate-N^1-(3-methyl)phenylthiosemicarbazone (MePh-Hmpt, used to prepare complexes **3** and **6**) were synthesised. Scheme 3 reports the structure of the used ligands.



Scheme 3. Schematic view of the used ligands.

2.3. Synthesis of the complexes

To a hot stirred methanolic 40 mL solution of the proper ligand was added an amount of solid $[Cu(PPh_3)_2NO_3]$ for **1** (0.502 g of the ligand, 2.47 mmol, and 1.606 g of metal salt, 2.47 mmol), for **2** (0.610 g of the ligand, 2.43 mmol, and 1.580 g of metal salt, 2.43 mmol), for **3** (0.484 g of the ligand, 1.82 mmol, and 1.187 g of metal salt, 1.82 mmol) together with additional 40 mL of methanol. Similarly, to a hot stirred methanolic 40 mL solution of the proper ligand was added an amount of solid $[Cu(PPh_3)_2CH_3COO]$ for **4** (0.610 g of the ligand, 3.00 mmol, and 3.890 g of metal salt, 6.00 mmol), for **5** (0.480 g of the ligand, 1.91 mmol, and 1.238 g of metal salt, 1.91 mmol), for **6** (0.505 g of the ligand, 1.91 mmol, and 1.233 g of metal salt, 1.91 mmol) together with additional 40 mL of methanol. The mixture was allowed to reach the reflux temperature. When the inorganic salt was completely dissolved, the resulting solution appeared dark yellow and was left under magnetic stirring for 2 h. The solution was then cooled down to room temperature and by slow evaporation of the solvent, crystals suitable for X-ray diffraction were obtained for complexes **1**, **2**, **4** and **6**.

2.3.1. $[Cu(PPh_3)_2(Et\text{-}Hmpt)]_2(NO_3)_2$ 1

Yield: 2.01 g, 75% (based on metal). Mp: 166 °C. FT-IR (KBr, cm^{-1}) 3443, m, 3214, m, ν (NH); 3053, m, ν ($CH_{aromatic}$); 2980, m, ν ($CH_{aliphatic}$); 1725, s, ν (CO); 1570, s, ν (CN); 1435, s, ν (NCS); 1384, s, ν (NO); 774, m, ν (CS). *Anal.* Calc. for $C_{86}H_{86}N_8O_{10}P_4S_2Cu_2$: C, 60.52; H, 5.08; N, 6.56; S, 3.76. Found: C, 60.52; H, 5.08; N, 6.56; S, 3.76%. ^1H NMR data (δ, ppm; DMSO–d_6): 1.14 (t, 3H, CH_3CH_2–), 2.12 (s, 3H, CH_3CN–), 3.60 (m, 2H, CH_3CH_2–), 3.76 (s, 3H, CH_3O–), 7.25 (t, b, 18H, PPh_3 $H_p + H_o$); 7.37 (t, 12H, PPh_3 H_m); 8.53 (bs, 1H, NH); 11.61 (s, 1H, C(S)NH).

2.3.2. $[Cu(PPh_3)_2(Ph\text{-}Hmpt)]NO_3$ 2

Yield: 1.69 g, 77% (based on metal). Mp: 168 °C. FT-IR (KBr, cm^{-1}) 2970, mw, ν ($CH_{aliphatic}$); 1731, s, ν (CO); 1563, s, ν (CN); 1435, s, ν (NCS); 1384, s, ν (NO); 743, m, ν (CS). *Anal.* Calc. for $C_{47}H_{43}N_4O_5P_2SCu$: C, 62.62; H, 4.81; N, 6.21; S, 3.55. Found: C, 62.54; H, 4.91; N, 6.52; S, 2.83%. ^1H NMR data (δ, ppm; DMSO–d_6): 2.25 (s, 3H, CH_3CN–), 3.75 (s, 3H, CH_3O–), 7.25 (t, b, 18H, PPh_3 $H_p + H_o$); 7.37 (t, 12H, PPh_3 H_m); 7.50–7.72 (m, 5H, aromatic ligand H), 10.05 (bs, 1H, NH); 11.46 (s, 1H, C(S)NH).

2.3.3. $[Cu(PPh_3)_2(MePh\text{-}Hmpt)]NO_3$ 3

Yield: 1.20 g, 72% (based on metal). Mp: 183 °C. FT-IR (KBr, cm^{-1}) 3052, m, ν ($CH_{aromatic}$); 2970, mw, ν ($CH_{aliphatic}$); 1720, s, ν (CO); 1567, s, ν (CN); 1435, s, ν (NCS); 1384, s, ν (NO); 744, m, ν (CS). *Anal.* Calc. for $C_{48}H_{45}N_4O_5P_2SCu$: C, 62.98; H, 4.95; N, 6.12; S, 3.50. Found: C, 63.16; H, 4.87; N, 6.45; S, 2.85%. ^1H NMR data (δ, ppm; DMSO–d_6): 2.18 (s, 3H, CH_3CN–), 2.31 (s, 3H, CH_3Ph), 3.76 (s, 3H, CH_3O–), 7.25 (t, b, 18H, PPh_3 $H_p + H_o$); 7.37 (t, 12H, PPh_3 H_m); 7.50–7.70 (m, 5H, aromatic ligand H), 10.11 (bs, 1H, NH); 11.40 (s, 1H, C(S)NH).

2.3.4. $[Cu_2(O_2CCH_3)(Et\text{-}pt)(PPh_3)_2] \cdot H_2O$ **4**

Yield: 5.38 g, 75% (based on metal). Mp: 178 °C. FT-IR (KBr, cm^{-1}) 3442, m, ν (NH); 1650, s, ν (C=O) pyruvate; 1618, m, ν (CN); 1567, m, ν (CO) coordinated carboxylates; 695, m, ν (CS). *Anal.* Calc. for $C_{44}H_{44}N_3O_5P_2SCu_2$: C, 57.70; H, 4.84; N, 4.59; S, 3.50. Found: C, 57.11; H, 4.76; N, 4.44; S, 3.50%.

2.3.5. $[Cu(Ph\text{-}mpt)(PPh_3)]$ **5**

Yield: 0.72 g, 65% (based on metal). Mp: 158 °C. FT-IR (KBr, cm^{-1}) 3400, mb, ν (NH); 3048, m, ($CH_{aromatic}$); 1735, m, ν (CO); 1564, m, ν (CN); 746, ms, ν (CS). *Anal.* Calc. for $C_{29}H_{27}N_3O_2PSCu$: C, 60.46; H, 4.72; N, 7.29; S, 5.57. Found: C, 59.98; H, 4.96; N, 7.01; S, 5.23%. ^1H NMR data (δ, ppm; DMSO–d_6): 2.20 (s, 3H, CH_3CN–), 3.75 (s, 3H, CH_3O–), 7.25 (t, b, 9H, PPh_3 $H_p + H_o$); 7.37 (t, 6H, PPh_3 H_m); 7.55–7.72 (m, 5H, aromatic ligand H), 10.08 (bs, 1H, NH).

2.3.6. $[Cu_2(MePh\text{-}mpt)_2(PPh_3)_2]$ **6**

Yield: 0.68 g, 60% (based on metal). Mp: 197 °C. FT-IR (KBr, cm^{-1}) 3400, mb, ν (NH); 3025, m, ($CH_{aromatic}$); 1715, m, ν (CO); 1610, m, ν (CN); 742, ms, ν (CS). *Anal.* Calc. for $C_{60}H_{58}N_6O_4P_2S_2Cu_2$: C, 61.06; H, 4.95; N, 7.12; S, 5.43. Found: C, 61.18; H, 4.87; N, 7.13; S, 5.73%. ^1H NMR data (δ, ppm; DMSO–d_6): 2.21 (s, 3H, CH_3CN–), 2.35 (s, 3H, CH_3Ph), 3.80 (s, 3H, CH_3O–), 7.25 (t, b, 9H, PPh_3 $H_p + H_o$); 7.35 (t, 6H, PPh_3 H_m); 7.55–7.70 (m, 5H, aromatic ligand H), 10.17 (bs, 1H, NH).

2.4. X-ray crystallography

Relevant data concerning data collection and details of structure refinement are summarized in Tables 1a and 1b. Intensity data for **1** were collected on a CAD4 diffractometer with Cu Kα radiation, those of **2** on a Philips PW1100 and those of **4** and **6** on a SMART 1000 Bruker AXS diffractometers with Mo Kα radiation. Data from crystals of compound **1** were affected by twinning and were not corrected for absorption, while for compounds **2**, **4** and **6** absorption corrections were carried out using the psi-scan procedure for the first and the SADABS [25] procedure for **4** and **6**. The crystals of compounds **4** and **6** gave very poor diffraction and data could be collected only up to 23.30° of theta. The structures were solved using direct methods (SIR-97 [26]). Refinements were carried out by full matrix least-squares cycles SHELXL97 [27] for all compounds. Most hydrogen atoms were calculated with standard geometry and refined in riding position. The program PARST [28] was employed for the geometrical description and PLUTON [29] and MERCURY [30] for the drawings.

Table 1a
Selected crystal data.

Compound	(**1**)	(**2**)
Formula	$C_{86}H_{86}Cu_2N_8O_{10}P_4S_2$	$C_{47}H_{43}Cu_1N_4O_5P_2S_1$
Molecular mass	1706.71	901.39
Space group	$Pca2_1$	$P2_1/n$
a (Å)	19.057(4)	14.205(4)
b (Å)	18.376(3)	32.117(8)
c (Å)	24.365(8)	9.952(2)
α (°)	90	90
β (°)	90	90.40(2)
γ (°)	90	90
V (Å^3)	8532(4)	4540(2)
Z	4	4
$F(000)$	3552	1872
D_{calc} (Mg/m^3)	1.329	1.319
μ (mm^{-1})	2.28	0.647
λ (Å)	1.54184	0.71069
Radiation	Cu Kα	Mo Kα
θ range (°)	3–67.02	3–30.05
hkl range	0, 21; 0, 20; −27, 27	−19, 19; −45, 45; 0, 14
Crystal size (mm)	0.4, 0.5, 0.5	0.3, 0.4, 0.5
No. of measured reflections	12779	26205
No. of unique reflections	12772	13240
No. of refined parameters	867	560
Max. and min. resolutions ΔF map (e Å^{-3})	0.55, −0.43	0.62, −0.77
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0678	0.0473
Rw_2	0.1811	0.1532
Weighting scheme	$1/[\sigma^2(F_o^2) + (0.125P)^2]$	$1/[\sigma^2(F_o^2) + (0.0741P)^2]$

$P = (\max(F_o^2,0) + 2F_c^2)/3$.

Table 1b
Selected crystal data.

Compound	(**4**)	(**6**)
Formula	$C_{44}H_{44}Cu_2N_3O_5P_2S_1$	$C_{120}H_{116}Cu_4N_{12}O_8P_4S_4$
Molecular mass	915.90	2360.53
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	11.841(3)	11.561(3)
b (Å)	12.276(3)	19.518(3)
c (Å)	16.896(4)	26.054(5)
α (°)	72.40(2)	94.61(1)
β (°)	79.65(3)	96.22(1)
γ (°)	68.23(2)	90.10(1)
V (Å^3)	2167.8(9)	5825(2)
Z	2	2
$F(000)$	944	2448
D_{calc} (Mg/m^3)	1.402	1.346
μ (mm^{-1})	1.15	0.91
λ (Å)	0.71069	0.71069
Radiation	Mo Kα	Mo Kα
θ range(°)	3–23.29	3–23.31
hkl range	−13, 13;−13, 13; −18, 18	−12, 12; −21, 21; −28, 28
Crystal size (mm)	0.1, 0.1, 0.4	0.2, 0.2, 0.5
No. of measured reflections	17480	44871
No. of unique reflections	6228	16694
No. of refined parameters	514	1225
Max. and min. resolutions ΔF map (e Å^{-3})	0.75, −0.38	0.93, −0.30
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0467	0.0650
Rw_2	0.1429	0.1431
Weighting scheme	$1/[\sigma^2(F_o^2) + (0.0963P)^2]$	$1/[\sigma^2(F_o^2) + (0.0383P)^2]$

$P = (\max(F_o^2,0) + 2F_c^2)/3$.

3. Results and discussion

3.1. Synthesis and spectroscopy

Ligands were synthesized according to the procedure reported in [24] and complexes by reacting these ligands with bis(triphenylphosphine)copper(I) nitrate and with bis(triphenylphosphine) copper(I) acetate. Both ligands and complexes were produced in good yields. In complexes **1**, **2** and **3**, obtained from the nitrate salt, the ligand is protonated while in complexes **4**, **5** and **6**, that are obtained from the acetate salt, it is deprotonated. The syntheses were carried out in methanol in order to deter possible problems arising from transesterification or hydrolysis processes that could modify the ligands. Compound **4** was isolated with difficulty and only after many attempts. The best conditions were found using a 2:1 ratio of ligand with respect to the metal content. Moreover, in comparison with the syntheses of the other complexes, compound **4** was exposed to atmospheric oxygen and moisture more than the other ones being recalcitrant to crystallize. The higher acetate content stabilizing the anionic form of the ligand, together with the increased acidity of the hydrazine nitrogen due to copper(I) oxidised to copper(II), promoted the hydrolysis of the methyl group from the ester improving the electrophilicity of the carboxyl carbon and speeding up the process of demethylation.

The ^1H NMR spectrum of complex **1** exhibits the NHC=S signal at about 11.40 ppm, showing that the ligand is present in its neutral form and the structure of the complex in the solid state persists in DMSO solution; the deshielded N*H*CH_2CH_3 signal at 8.53 ppm upon complexation can be related to the change from an *E* to a *Z* conformation of the ligand and the coordination to the metal of the S and N3 atoms of the ligand [24]. Even for complexes **2** and **3** the signal attributed to NHC═S and the deshielded resonance of the N*H*R nucleus reveals that the ligands are in their neutral form and in a *Z* conformation showing that the three complexes behave in a similar way. The ^{1}H NMR spectra of complexes **4** and **5** show the lack of the signal of the N*H*C═S group confirming that in solution the ligand is deprotonated. The resonances at *ca* 10.10 ppm, downfield with respect to the resonances of the same N*H* group in the free ligand, show that also these compounds are in a *Z* conformation. Due to its paramagnetism, it was not possible to record the ^{1}H NMR spectra of complex **4**. As regards as IR spectra, the absorptions in the region 3510–3150 cm^{-1} usually attributed to *ν*(OH) and *ν*(NH) stretching frequencies are assigned with difficulty, because of numerous hydrogen bonding interactions involving amino and imino groups (NH···S, NH···ONO_2^- and NH···OH_2). No relevant shifts are observed by the comparison of the vibrational stretching C═O bonds of complexes with the absorption of the free ligands [24], showing that the metal centre does not bind via pyruvate oxygen. An exception is reported for complex **4**, where the C═O absorption at 1650 cm^{-1} (*ca* 70 cm^{-1} at lower frequencies with respect the free ligand) shows that the C═O group is involved in coordination. For all complexes *ν*(C═N) and *ν*(C═S) are significantly shifted at lower frequencies showing that every ligand bind the metal ion via N,S. For complexes **1**, **2** and **3** the nitrate group vibration can be easily find at 1384 cm^{-1} with a strong absorption, while for complex **4**, the typical stretching bands (symmetrical and asymmetrical) for CH_3COO^- are identified. In agreement with diffraction and/or NMR data, no counterion can be observed in the IR spectra of compounds **5** and **6**.

An electron paramagnetic resonance study was also performed for compound **4** in order to provide information about the electronic structure of the metal and its immediate surrounding. The sample was in polycrystalline form because we experienced some difficulty to find single crystals of dimensions large enough to give an acceptable signal to noise ratio. The resulting derivative absorptions, with superimposed a DPPH (diphenyl-β-picrylhydrazyl) marker ($g = 2.0036$), are shown in Fig. 1a and b. The two spectra are quite similar, apart from the observation at the liquid nitrogen temperature of a more intense signal with some emphasization of a number of not completely resolved weak peaks of a possible superhyperfine nature, see below. The increase of the peak-to-peak intensity in decreasing temperature is usual in EPR, reminiscent of the fact that a simple isolated paramagnetic centre follows the 1/*T* Curie's law.

Both resonance signals appear typical for a Cu^{2+} ion in octahedral field with tetragonal distortion and show a well resolved four lines hyperfine pattern in the low field range. They may be described by a spin Hamiltonian of the form:

$$\mathscr{H} = \mu_B \vec{S}\cdot\overset{\leftrightarrow}{g}\cdot\vec{H} + \vec{S}\cdot\overset{\leftrightarrow}{A}\cdot\vec{I}, \quad \text{with } S = 1/2,\ I_{Cu} = 3/2. \qquad (1)$$

Here the first term represents the Zeeman interaction of the copper unpaired spin $S = 1/2$ with the applied static magnetic field *H* (μ_B = Bohr magneton) and the second one describes the hyperfine interaction of the unpaired electron with the copper nucleus ($I = 3/2$).

The $\overset{\leftrightarrow}{g}$ and $\overset{\leftrightarrow}{A}$ tensors are approximately axial with maximum values:

$$g_{//} = 2.274 \pm 0.002 \quad \text{and} \quad |A_{//}| = (104 \pm 2) \times 10^{-4}\ \text{cm}^{-1} \qquad (2)$$

However, the presence of a rhombic contribution is also evident, more pronounced in the high temperature spectrum, but the overlap of various non-resolved hyperfine peaks prevents a precise determination of the in-plane constants.

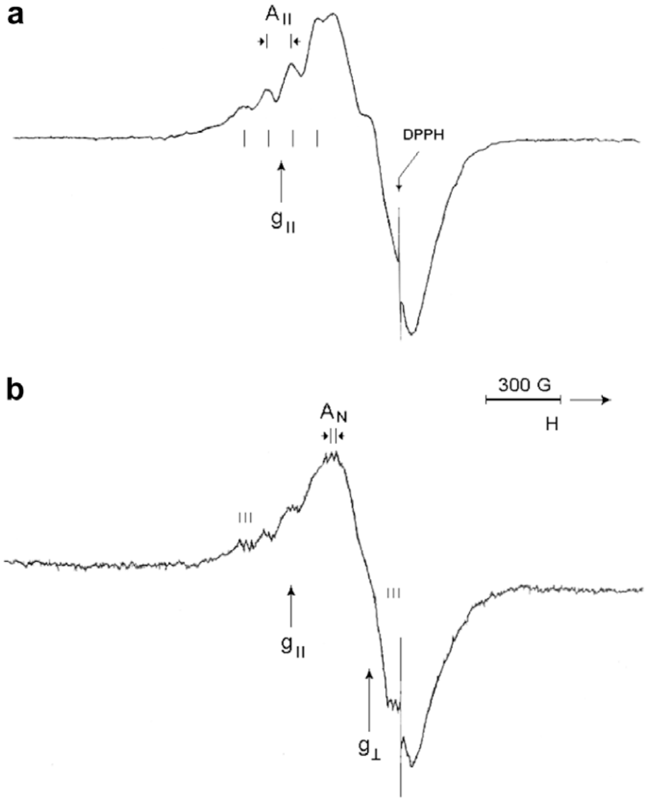


Fig. 1. Derivative X-band EPR spectra of a polycrystalline sample of **4** at room temperature (a) and at *T* = 77 K (b). The observed intensities of the signals a and b were in the approximate ratio 1:4.

Assuming complete axial symmetry, we estimate:

$$g_{\perp} \approx 2.065 \pm 0.007 \quad \text{and} \quad |A_{\perp}| \leqslant 30 \times 10^{-4}\ \text{cm}^{-1} \qquad (3)$$

Although in general the measured *g* values may not coincide with the local single-ion values if exchange is present, here we have no doubt about this because the $\bar{1}$ point symmetry makes the two copper(II) per unit cell magnetically undistinguishable.

The *g* values are strongly indicative of a magnetically isolated Cu^{2+} ion with unpaired spin in a substantially $d_{x^2-y^2}$ ground state orbital. In this case, in fact, it should roughly be [31]:

$$\begin{aligned} g_{//} &= g_0 - 8\alpha^2\lambda/\Delta_1, \\ g_{\perp} &= g_0 - 2\alpha^2\lambda/\Delta_2, \end{aligned} \qquad (4)$$

where g_0 is the free electron g value 2.0023, *λ* is the spin-orbit coupling constant for the free copper ion with a vale close to −828 cm^{-1}, and Δ_1 and Δ_2 stand for the optical energy splittings due to the crystal-field between the ground state and the d_{xy} and $d_{xz,yz}$ orbitals, respectively.

The reducing α^2 factor measures the fraction of time spent by the unpaired electron at the copper ion and is directly related to the covalence of the bonds [32–34]. A light anisotropy of this factor arising from the excited orbitals d_{xy} and $d_{xz,yz}$ in (Eq. (4)) has been neglected for simplicity.

The value $|A_{//}|$ appears somewhat low as compared with usual axial values for copper(II) complexes, frequently found in the range 150–200 × 10^{-4} cm^{-1}. The reduced value has possibly to be related to the strong spin delocalization due to the Cu(II)–S very covalent bond. In fact, this should result in two distinct effects. A low presence of the unpaired spin at the copper nucleus with reduction of both the dipolar and Fermi-contact terms of the hyperfine interaction, and an induced in-plane rhombic distortion with mixing between the $d_{x^2-y^2}$

and $d_{3z^2-r^2}$ orbitals which should also reduce the axial dipolar term [34].

As a further experimental fact, we observe that the powder spectrum at liquid nitrogen temperature shows the presence of several groups of three equiintense weak peaks, see Fig. 1b. The measured splittings correspond to energies in the range 13–16 × 10^{-4} cm^{-1}. Both the number of peaks and the energy splitting involved seem to suggest the presence of a superhyperfine interaction between the magnetic copper and one nitrogen nucleus ($I_N = 1$), in line with the structure of Fig. 5.

In conclusion, all the results of this EPR study on a polycrystalline sample of compound **4** appear to strictly support the proposed crystallographic view based on two copper centres in different oxidation states.

3.2. Crystal structures of the complexes

A PLUTON drawing representing complex $[Cu(PPh_3)_2(Et\text{-}Hmpt)]_2(NO_3)_2$ **1** is reported in Fig. 2. The structure can be described as formed by two cationic complex molecules with two bridging nitrates that act as counterions. The copper(I) ion coordinates two triphenylphosphines and an N^1-ethyl methylpyruvate thiosemicarbazone molecule in its neutral form. The thiosemicarbazones bind to the metal through the sulfur and the iminic nitrogen and form a five-term chelation ring. The coordination bonds have distances of 2.165(6) and 2.148(6) Å for the Cu–N bonds and 2.365(2) and 2.368(2) Å for the Cu–S bonds. The Cu–P bonds range instead from 2.254(2) to 2.281(2) Å. The angles N–Cu–S of 82.3(2)° and 82.9(2)° are fairly small, while the P–Cu–P angles are wide (129.60(8)° and 130.54(8)°). The copper coordination is slightly distorted from the ideal tetrahedron but less than expected in the presence of a potentially terdentate planar ligand. The non-methylated oxygens of the ligand and the copper atom are 2.802(6) and 2.799(6) Å apart and do not seem to influence the copper coordination geometry. Noteworthy in both molecules that the centroids between the coordinated N and S atoms lie on the plane defined by P–Cu–P, as in a typical tetrahedral coordination geometry.

The thiosemicarbazone moieties, expected to be planar because of the extended conjugated system of double bonds, in one of the cations are in fact fairly planar with a distortion of only 9.8(4)° between the average thiosemicarbazide plane and that of the terminal carboxylate, but in the other the molecule are significantly distorted: the angle between the average plane of the terminal carboxylate and that of the thiosemicarbazide fragment is 23.0(4)°.

Table 2
Selected parameters of the hydrogen bonds involving the nitrate ions in compound **1**.

Donor···acceptor (Å)	Angle (°)	Donor···acceptor (Å)	Angle (°)
N1···O4	N1–H1···O4	N1A···O4	N1A–H1A···O4
3.01(2)	149.5(6)	3.18(1)	131.6(6)
N1···O6	N1–H1···O6	N1A···O6	N1A–H1A···O6
2.87 (1)	134.0(6)	3.17(2)	139.3(6)
N2···O4	N2–H2···O4	N2A···O4	N2A–H2A···O4
3.18(2)	135.9(5)	3.13(1)	137.4(5)
N2···O6	N2–H2···O6	N2A···O6	N2A–H2A···O6
3.19(1)	131.6(4)	2.85(1)	142.6(5)

A peculiarity of this structure is the way the two nitrate ions link the two cationic moieties. A system of loose bifurcated hydrogen bonds binds each thiosemicarbazone amino and hydrazine NH groups to two different oxygen atoms from the nitrate ions (see Fig. 2). These interactions are quite loose and this is reflected in the long bond distances (see Table 2) observed in the structure and also in the high thermal parameters presented by the nitrate ions.

Another feature that characterizes the packing of these molecules is a sixfold phenyl embrace (6PE) [35–38] (P1···P1^I $I = (x, 1 + y, z)$ distance 7.354 Å) (see Fig. 3) between molecules related by a translation along y. More precisely the phenyls of the triphenylphosphines involved in this interaction present what the aforementioned paper calls an “offset sextuple phenyl embrace” (OSPE) conformation. To complete the description of the packing it is noteworthy to observe that the hydrogen bonds with the nitrate ions together with these OSPE create a ribbon of molecules that develops along the y-axis.

The structure of compound **2**, $[Cu(PPh_3)_2(Ph\text{-}Hmpt)]NO_3$, is reported in Fig. 4. The asymmetric unit is formed by a complex cation, $[Cu(PPh_3)_2(Ph\text{-}Hmpt)]^+$, and a disordered nitrate anion bound through a loose charge-assisted hydrogen bond. In the cation complex, the copper(I) ion coordinates two triphenylphosphines and an N^1-phenyl methylpyruvate thiosemicarbazone molecule in its neutral form. Also in this case the thiosemicarbazone binds to the metal through the sulfur and the iminic nitrogen and forms a five-term chelation ring. The angle N–Cu–S is 81.70(7)° while the

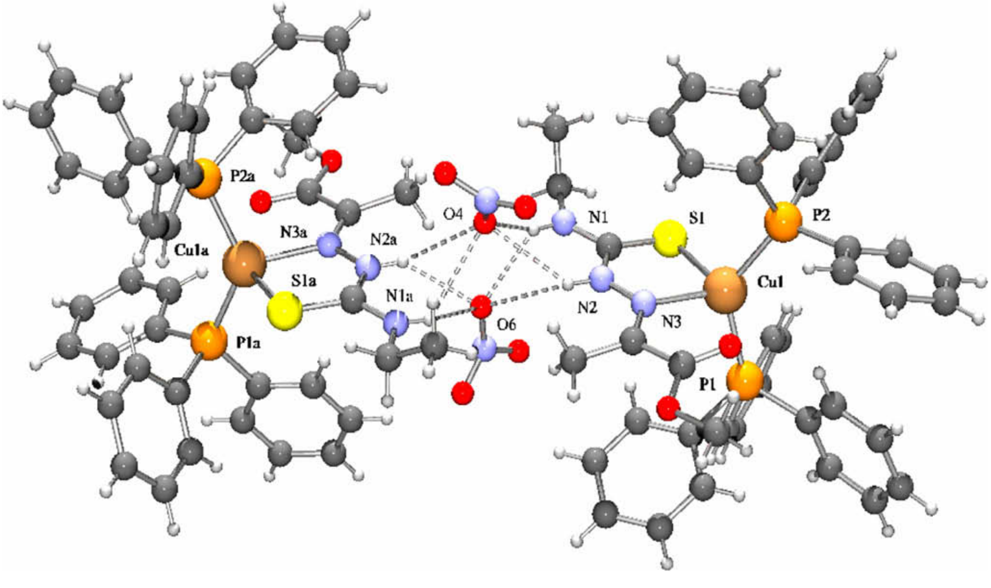


Fig. 2. PLUTON rendering of complex $[Cu(PPh_3)_2(Et\text{-}Hmpt)]_2(NO_3)_2$ **1**.

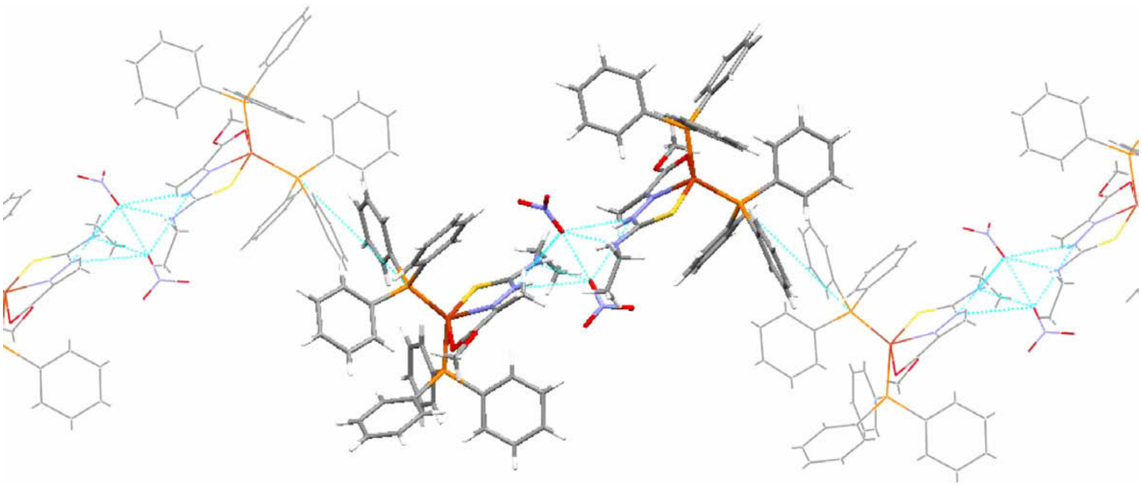


Fig. 3. MERCURY drawing showing compound **1** with two adjacent molecules linked through the six phenyl embrace.

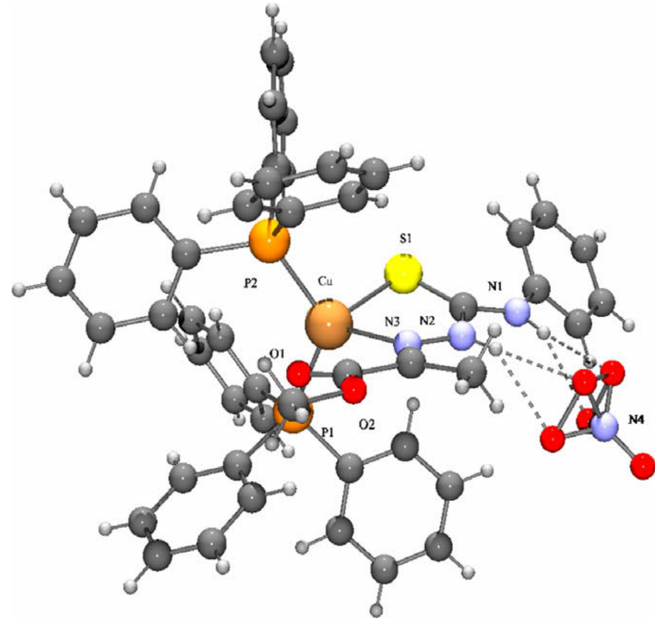


Fig. 4. PLUTON rendering of complex $[Cu(PPh_3)_2(Ph\text{-}Hmpt)]NO_3$ **2** showing the disordered nitrate hydrogen bond interaction (on the right-hand side).

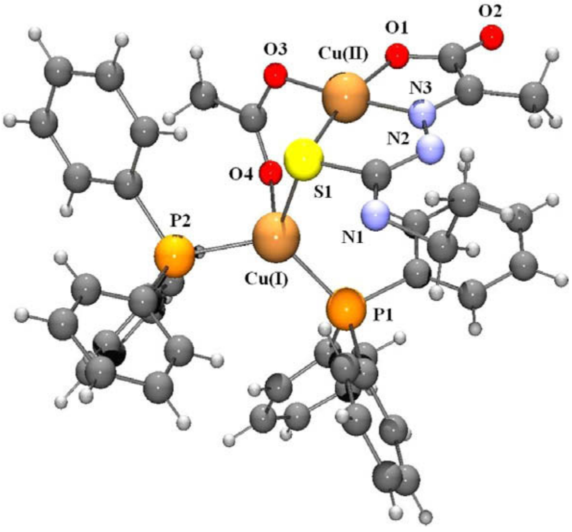


Fig. 5. PLUTON rendering of compound **4** complex fragment $[Cu_2(O_2CCH_3)(Et\text{-}pt)(PPh_3)_2]$.

P–Cu–P is slightly narrower than the previous ones, being 124.28(3)°. Compared to compound **1** the copper tetrahedral coordination is therefore slightly more regular. The coordination bonds have values of 2.156(2) Å for Cu–N, 2.400(1) Å for Cu–S and the Cu–P bonds are of 2.282(1) and 2.277(1) Å.

The thiosemicarbazone ligand is strongly distorted from the expected planarity and the angle between the thiosemicarbazide average plane and that of the carboxylate fragment is of 24.10(9)°; also the average plane of the phenyl ring is tilted of 36.3(1)° with respect to the thiosemicarbazide group. Also here, one carboxylate oxygen is oriented in the direction of the copper atom but presents a long distance Cu–O of 2.780(2) Å.

The crystal structure of compound **4** $[Cu_2(O_2CCH_3)(Et\text{-}pt)(PPh_3)_2] \cdot H_2O$ is reported in Fig. 5. The solution of this structure shed light on the anomalies that were observed in the elemental analysis and the IR spectra. This compound was particularly recalcitrant to crystallise and, probably due to the long exposure to oxygen and to air moisture, copper(I) has been partially oxidised to copper(II) and the ligand has hydrolysed and lost the ester methyl group and has become a carboxylic acid. The asymmetric unit, as a consequence, contains two metal centres in two different oxidation states. The two copper atoms are bridged by an acetate ion and by a shared sulfur from the thiosemicarbazone. The copper(II) atom coordinates in a square planar fashion the thiosemicarbazone ligand. In this case the ligand behaves as O,N,S terdentate using also its carboxylic oxygen. The fourth position site is occupied by an acetate oxygen atom. The coordination distances are: Cu(II)–N 1.912(4), Cu(II)–S 2.267(1), Cu(II)–O 1.949(3) and Cu(II)–O(ac) 1.895(3) Å. Those of the tetrahedral copper(I) fragment are: Cu(I)–O(ac) 2.248(4), Cu(I)–S1 2.351(1) Å, and the two with the phosphorus atoms of the tpp ligands are Cu–P1 2.238(1) and Cu–P2 2.277(1) Å.

The packing is formed by ribbons of molecules held together by hydrogen bonds involving the water molecule [N1–H···O1 W 2.936(7) Å 158.8(4)° and O1 W···O1W^{i} 2.982(7) Å i = $-x, -y, -z + 2$] and by a weak interaction between the copper(II) atom with the hydrazine nitrogen atom of a nearby molecule (Cu2···N2^{i} 3.406(5) Å i = $-x + 1, -y, -z + 2$) as can be seen in Fig. 6. These ribbons are then joined together by a 6PE (sixfold phenyl embrace)

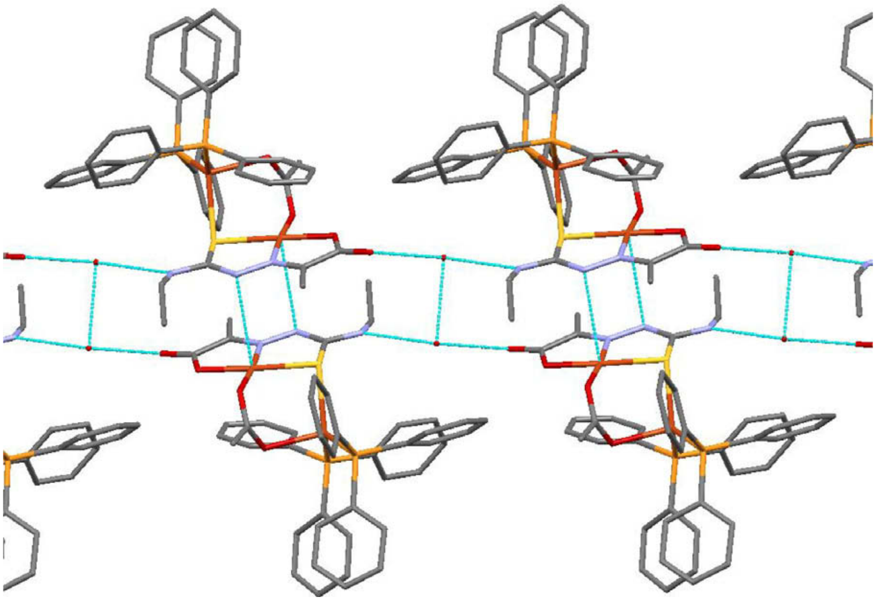


Fig. 6. MERCURY drawing of the packing of compound **4** showing the ribbon of complex molecules held together through hydrogen bonds formed by water molecules and by a long interaction between copper(II) and the hydrazine nitrogen of an adjacent molecule.

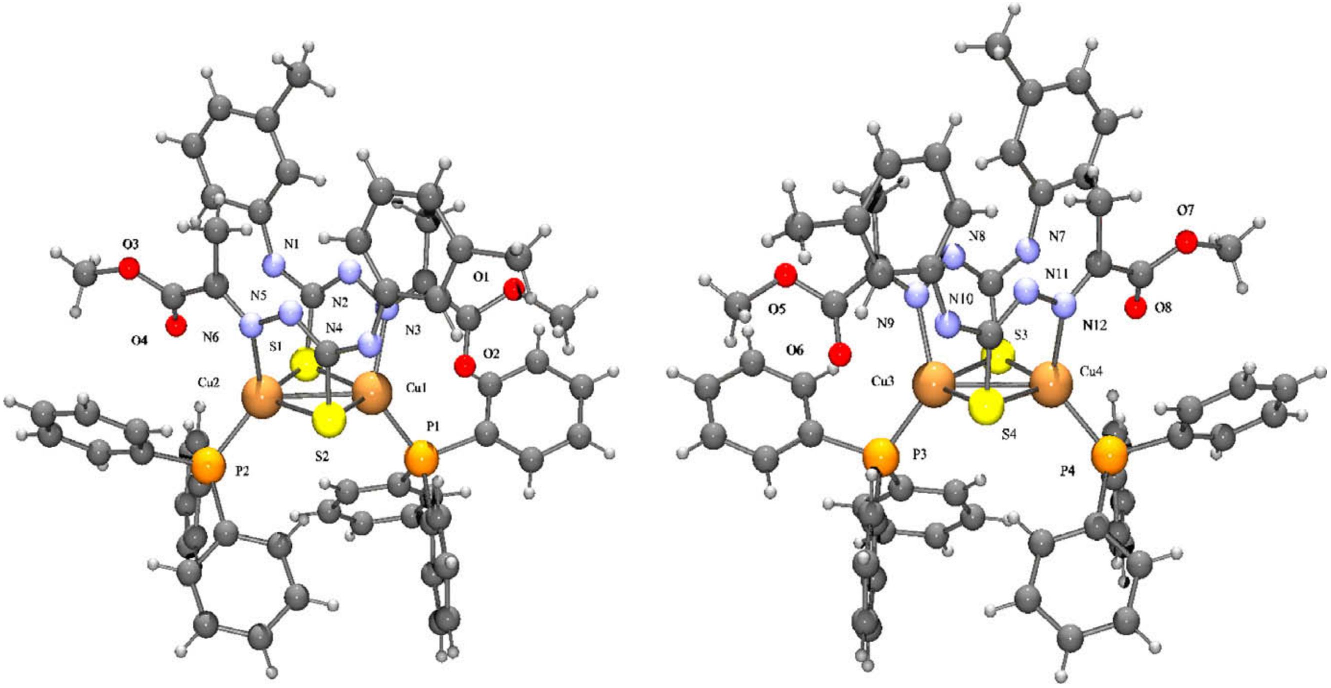


Fig. 7. PLUTON rendering of the two independent molecules of complex $[Cu_2(MePh\text{-}mpt)_2(PPh_3)_2]$ **6**.

Table 3
Selected bond distances for compound **6**.

Bond	Distance (Å)	Bond	Distance (Å)
Cu1–Cu2	2.845(1)	Cu3–Cu4	2.845(1)
Cu1–S1	2.347(3)	Cu3–S3	2.343(3)
Cu1–S2	2.379(3)	Cu3–S4	2.386(3)
Cu1–P1	2.213(3)	Cu3–P3	2.207(3)
Cu1–N3	2.102(7)	Cu3–N9	2.084(7)
Cu2–S1	2.385(3)	Cu4–S3	2.395(3)
Cu2–S2	2.343(3)	Cu4–S4	2.343(3)
Cu2–P2	2.217(3)	Cu4–P4	2.213(3)
Cu2–N6	2.124(7)	Cu4–N12	2.115(8)

interaction with a distance P···P of 7.234 Å that involves the triphenylphosphines.

The crystal structure of compound **6** $[Cu_2(MePh\text{-}mpt)_2(PPh_3)_2]$ is reported in Fig. 7. The asymmetric unit contains two independent enantiomeric complex molecules. Both are planar 2Cu–2S clusters made up of two copper ions with interatomic distances of 2.845(1) and 2.844(1) Å, bridged by two sulfur atoms belonging to two thiosemicarbazone ligands. These ligands are deprotonated and located on the same face of the cluster plane, bind through the sulfur and the iminic nitrogen (see Table 3) and are perpendicular to each other and oriented head to tail (see Fig. 7). The triphenylphosphines are on the opposite side and two phenyls interact edge

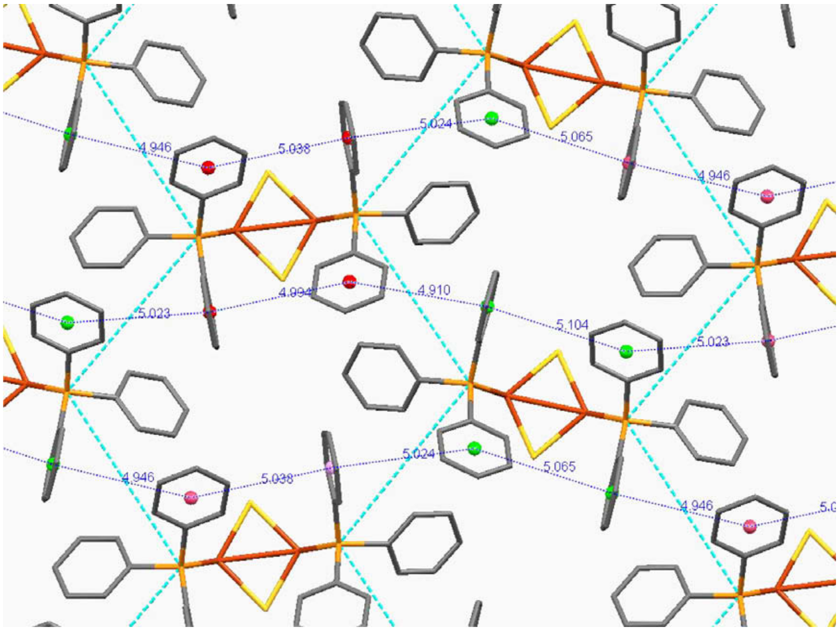


Fig. 8. MERCURY drawing of the packing of compound **6** showing the phenyl–phenyl edge to face interactions extending in the *xy* plane.

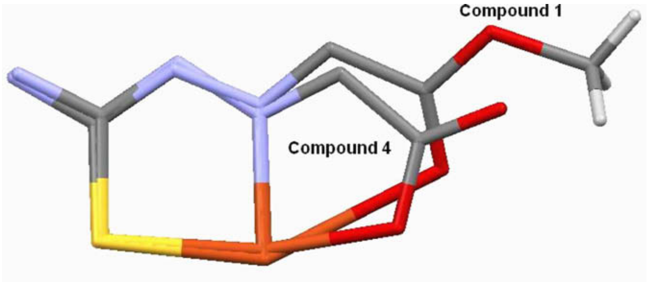


Fig. 9. PLUTON rendering of the methylpyruvate thiosemicarbazone group deformation observed passing from a Cu(I) in **1** to a Cu(II) coordination in **4**.

to face with those of an adjacent molecule forming parallel quadruple phenyl embrace (PQPE) [35–38] (see Fig. 8).

4. Conclusions

Copper(I) ions, with their d^{10} electronic configuration, 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, in bistriphenylphosphine complexes present in the Cambridge Structural Database [39], is usually occupied by a fourth ligand, usually a halide. In previous experiments we have verified that the absence of other soft species can influence the coordination and in particular that the imino nitrogen can become a suitable donor for coordination on a soft metal ion in the absence of softer competitors. What is apparent in the structures reported in this paper is that the control on the coordinating behaviour of a ligand is tuned by a series of factors among which the predominant is the hard soft nature of the atoms involved in the interactions with the metal centre. In our case it is striking the comparison between compounds **1** and **4**. Compound **4** was recalcitrant to crystallisation and the crystals were obtained after many attempts leaving the compound exposed to atmospheric oxygen and moisture. The copper(I) oxidised to copper(II) increases both the acidity of the hydrazine nitrogen stabilizing the anionic form and promotes the hydrolysis of the methyl group from the esther improving the electrophilicity of the carboxyl carbon and speeding up the process of demethylation. This phenomenon of demethylation had been previously observed in a work where an analogous ligand was coordinated by zinc(II) [40]. The ligand is therefore the same but the effects are dramatically different in the coordination of copper(I) versus copper(II). The fairly rigid ligand is markedly deformed upon coordination on copper(II) in **4** (see Fig. 9) to allow the carboxylic oxygen to bind to the metal ion, while it remains almost unaltered upon coordination of copper(I) in **1**.

Acknowledgment

Thanks are due to Dr. Mario Ghillani for his valuable contribution in the recording of EPR spectra.

Appendix A. Supplementary data

CCDC 690657, 690658, 690659 and 690660 contains the supplementary crystallographic data for compounds **1**, **2**, **4** 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.2009.01.013.

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