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# Copper(I)–organophosphine complexes of bis(3,5-dimethylpyrazol-1-yl)dithioacetate ligand

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#### Abstract

Copper(I) complexes have been synthesized from the reaction of CuCl, monodentate tertiary phosphines PR<sub>3</sub> (PR<sub>3</sub> = P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>; P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(4-C<sub>6</sub>H<sub>4</sub>COOH); P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(2-C<sub>6</sub>H<sub>4</sub>COOH); PTA, 1,3,5-triaza-7-phosphaadamantane; P(CH<sub>2</sub>OH)<sub>3</sub>, tris(hydroxymethyl)phosphine) and lithium bis(3,5-dimethylpyrazolyl)dithioacetate, Li[LCS<sub>2</sub>]. Mono-nuclear complexes of the type [LCS<sub>2</sub>]Cu[PR<sub>3</sub>] have been obtained and characterized by elemental analyses, FT-IR, ESI-MS and multinuclear (<sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P) NMR spectral data; in these complexes the ligand behaves as a  $\kappa^3$ -*N*,*N*,*S* scorpionate system. One exception to this stoichiometry was observed in the complex [LCS<sub>2</sub>]Cu[P(CH<sub>2</sub>OH)<sub>3</sub>]<sub>2</sub>, where two phosphine co-ligands are coordinated to the copper(I) centre. The solid-state X-ray crystal structure of [LCS<sub>2</sub>]Cu[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>] has been determined. The [LCS<sub>2</sub>]Cu[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>] complex has a pseudo tetrahedral copper site where the bis(3,5-dimethylpyrazolyl)dithioacetate ligand acts as a  $\kappa^3$ -*N*,*N*,*S* donor.

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Keywords: Copper(I); Scorpionates; X-ray; Phosphines; Spectroscopy

#### 1. Introduction

It is known that copper is an essential trace metal for living organisms [1]. This metal plays a crucial role in different enzymes that catalyze oxidation/reduction reactions involved with the antioxidant system of the organism [2]. It has been reported that certain copper-complexes catalyze radical formation while others seem to have efficacy as antioxidants [3]. The different behaviour depends upon the chemical environment and nature of the chelating agent. In this field, our attention has been focused on copper(I) complexes containing "scorpionate" ligands [4–8]. Poly(pyrazolyl)borates [9] and related scorpionates [10]

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have been extensively employed as anionic  $\sigma$ -donor ligands in a variety of metal complexes, and they have found wide application in coordination, organometallic and bioinorganic chemistry [11]. Modifications of poly(pyrazolyl)borates can be made by replacement of the boron bridging atom by other elements such as carbon [12], silicon [13] or phosphorus [14,15]. Recent contributions are related to the ligands derived from bis(pyrazol-1-yl)methane, with [RR'C(pz)<sub>2</sub>] as general structure and bearing a coordinating moiety (R') such as acetate [6,8,16–34] or dithioacetate [21,23,26,33,35–37].

On this basis, in recent years, we have focused our attention on the study of the coordinative ability of the mono-anionic heteroscorpionate bis(pyrazol-1-yl)acetate [6,8,16,22–24] and bis(pyrazol-1-yl)dithioacetate [23,37] ligands, towards Cu(I), Re(V) and Sn(IV) acceptors. As part of our investigations into the copper(I) coordination

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chemistry [4-8], here we describe the synthesis and structural characterization of new pyrazole-based scorpionate copper(I) complexes containing monodentate tertiary phosphine co-ligands.

# 2. Experimental

All reagents were purchased from Alfa (Karlsruhe) and Aldrich (Milwaukee) and used as received. The ligand lithbis(3,5-dimethylpyrazolyl)dithioacetate, ium Li[LCS<sub>2</sub>] (Fig. 1), was prepared according to the literature methods [35]. All syntheses and handling were carried out under an atmosphere of dry, oxygen-free dinitrogen, using standard Schlenk techniques or a glove box. All solvents were dried, degassed and distilled prior to use. Elemental analyses (C, H, N, S) were performed in house with a Fisons Instruments 1108 CHNS-O Elemental Analyser. Melting points were taken on an SMP3 Stuart Scientific Instrument. IR spectra were recorded from 4000 to  $100 \text{ cm}^{-1}$ with a Perkin-Elmer System 2000 FT-IR Instrument. IR annotations used: m = medium, mbr = medium broad, s = strong, sbr = strong broad, sh = shoulder, w = weak. <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded on a Oxford-400 Varian spectrometer (400.4 MHz for <sup>1</sup>H and 162.1 MHz for  ${}^{31}$ P). NMR annotations used: d = doublet, dd = double doublet, dbr = broad doublet, m = multiplet, m = broadmultiplet, s = singlet, sbr = broad singlet, t = triplet. Electrospray ionization mass spectra (ESIMS) were obtained in positive- or negative-ion mode on a Series 1100 MSD detector HP spectrometer using a methanol mobile phase. The compounds were added to the reagent grade methanol to give solutions of approximate concentration 0.1 mM. These solutions were injected  $(1 \mu l)$  into the spectrometer via a HPLC HP 1090 Series II fitted with an autosampler. The pump delivered the solutions to the mass spectrometer source at a flow rate of 300  $\mu$ l min<sup>-1</sup>, and nitrogen was employed both as a drying and nebulizing gas. Capillary voltages were typically 4000 V and 3500 V for the positiveand negative-ion mode, respectively. Confirmation of all major species in this ESIMS study was aided by comparison of the observed and predicted isotope distribution patterns, the latter calculated using the ISOPRO 3.0 computer program.



Fig. 1. Schematic representation of the ligand Li[LCS<sub>2</sub>].

#### 2.1. Synthesis

# 2.1.1. $[LCS_2]Cu[P(C_6H_5)_3]$ (1)

To a methanol/acetonitrile (1:5) solution (50 ml) of CuCl (0.099 g, 1.0 mmol) and  $P(C_6H_5)_3$  (0.262 g, 1.0 mmol), the ligand lithium bis(3,5-dimethylpyrazolyl)dithioacetate, Li[LCS<sub>2</sub>], (0.286 g, 1.0 mmol) was added at room-temperature. After addition, the reaction mixture was stirred for 12 h, and the solvent was removed under vacuum. The resulting solid was treated with chloroform (50 ml) and the salt (LiCl) removed by filtration. The filtrate was concentrated under vacuum and an orange solid was filtered off, washed with diethyl ether and re-crystallized from  $CHCl_3/n$ -hexane (1:3) to give complex 1 in 86% yield. M.p. 187 °C dec. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 293 K):  $\delta$ 1.73 (s, 6H, 3-CH<sub>3</sub>), 2.50 (s, 6H, 5-CH<sub>3</sub>), 5.87 (s, 2H, 4-CH), 7.30-7.64 (m, 16H, CH). <sup>1</sup>H NMR (DMSO, 293 K):  $\delta$  1.69 (s, 6H, 3-CH<sub>3</sub>), 2.45 (s, 6H, 5-CH<sub>3</sub>), 6.09 (s. 2H, 4-CH), 7.35-7.52 (m, 15H, CH), 7.41 (m, 1H, CHCS<sub>2</sub>).  ${}^{13}C{}^{1}H{}$  NMR (CDCl<sub>3</sub>, 293 K):  $\delta$  11.90 (5-CH<sub>3</sub>), 13.91 (3-CH<sub>3</sub>), 79.36 (CHCS<sub>2</sub>), 106.67 (4-CH), 128.71-134.33 ( $C_6H_5$ ), 140.82 (5-CCH<sub>3</sub>), 148.82 (3-CCH<sub>3</sub>).  ${}^{31}P{}^{1}H{}$  NMR (CDCl<sub>3</sub>, 293 K):  $\delta$  7.08 (s). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 218 K):  $\delta$  6.91 (sbr). IR (nujol, cm<sup>-1</sup>): 3052w (CH); 1557s (C=N, C=C); 1094s, 1060s  $(v_{asym}CS_{2}^{-});$  876s, 850s, 814m, 791m  $(v_{sym}CS_{2}^{-});$  529s, 509s, 491s (R<sub>3</sub>P); 447m, 435m, 428m, 418m, 379w, 340w; 299w (Cu–N). ESIMS (major positive-ions, CH<sub>3</sub>OH), m/z(%): 931 (100)  $[\{(LCS_2)Cu[P(C_6H_5)_3]_2 + Cu\}]^+$ . ESIMS (major negative-ions, CH<sub>3</sub>OH), m/z (%): 279 (100) [LCS<sub>2</sub>]<sup>-</sup>. Anal. Calc. for C<sub>30</sub>H<sub>30</sub>CuN<sub>4</sub>PS<sub>2</sub>: C, 59.54; H, 5.00; N, 9.26; S, 10.59. Found: C, 59.39; H, 5.08; N, 9.08; S, 10.36%.

#### 2.1.2. $[LCS_2]Cu[P(C_6H_5)_2(4-C_6H_4COOH)]$ (2)

Complex 2 was prepared analogously to compound 1 by using CuCl (0.099 g, 1.0 mmol), [P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(4-C<sub>6</sub>H<sub>4</sub>COOH)] (0.306 g, 1.0 mmol) and Li[LCS<sub>2</sub>] (0.286 g, 1.0 mmol) in methanol/acetonitrile (1:5) solution (50 ml). The orange product was re-crystallized from chloroform/n-hexane (1/3), in 80% yield. M.p. 164 °C dec. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 293 K): δ 1.71 (s, 6H, 3-CH<sub>3</sub>), 2.49 (s, 6H, 5-CH<sub>3</sub>), 5.93 (s, 2H, 4-CH), 7.25–8.05 (m, 15H, CH). <sup>1</sup>H NMR (DMSO, 293 K): δ 1.69 (s, 6H, 3-CH<sub>3</sub>), 2.45 (s, 6H, 5-CH<sub>3</sub>), 6.09 (s, 2H, 4-CH), 7.31-8.00 (m, 14H, CH), 7.41 (m, 1H, CHCS<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 293 K):  $\delta$  7.18 (sbr). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 218 K):  $\delta$  7.16 (sbr). IR (nujol, cm<sup>-1</sup>): 3405br (OH); 3048w (CH); 1694sbr (C=O); 1560s (C=N, C=C); 1094s, 1019s ( $v_{asym}CS_2^{-}$ ); 873s, 850s ( $v_{sym}CS_2^{-}$ ); 567w, 540sbr, 516sbr (R<sub>3</sub>P); 441br, 398w, 375w, 352w, 326w; 303w (Cu-N). ESIMS (major positive-ions, CH<sub>3</sub>OH), m/z (%): 650 (20) [{(LCS<sub>2</sub>)Cu[P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(4-C<sub>6</sub>  $H_4COOH$ ] + H]<sup>+</sup>, 1019 (100) [{(LCS<sub>2</sub>)Cu[P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(4- $C_6H_4COOH)_2 + Cu\}^+$ . ESIMS (major negative-ions, CH<sub>3</sub>OH), m/z (%): 378 (100) [{(LCS<sub>2</sub>)Cu + Cl}]<sup>-</sup>. Anal. Calc. for C<sub>31</sub>H<sub>30</sub>CuN<sub>4</sub>O<sub>2</sub>PS<sub>2</sub>: C, 57.35; H, 4.66; N, 8.63; S, 9.88. Found: C, 57.19; H, 4.54; N, 8.78; S, 10.02%.

# 2.1.3. $[LCS_2]Cu[P(C_6H_5)_2(2-C_6H_4COOH)]$ (3)

Complex 3 was prepared analogously to compound 1 by using CuCl (0.099 g, 1.0 mmol),  $[P(C_6H_5)_2(2-C_6H_4COOH)]$ (0.306 g, 1.0 mmol) and Li[LCS<sub>2</sub>] (0.286 g, 1.0 mmol) in methanol/acetonitrile (1:5) solution (50 ml). The orange product was re-crystallized from chloroform/n-hexane (1/ 3), in 75% yield. M.p. 192 °C dec. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 293 K): δ 1.68 (s, 6H, 3-CH<sub>3</sub>), 2.47 (s, 6H, 5-CH<sub>3</sub>), 5.93 (s, 2H, 4-CH), 7.25-8.05 (m, 15H, CH). <sup>1</sup>H NMR (DMSO, 293 K): δ 1.67 (s, 6H, 3-CH<sub>3</sub>), 2.44 (s, 6H, 5-CH<sub>3</sub>), 6.08 (s, 2H, 4-CH), 7.29-8.00 (m, 14H, CH), 7.40 (m, 1H, CHCS<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 293 K):  $\delta$  0.78 (br). <sup>31</sup>P{<sup>1</sup>H} NMR  $(CDCl_3, 218 \text{ K})$ :  $\delta 0.91$  (s). IR (nujol, cm<sup>-1</sup>): 3451br (OH); 3124w, 3053w (CH); 1658sbr (C=O); 1558s (C=N, C=C); 1080m, 1039w ( $v_{asym}CS_2^{-}$ ); 874s, 849m, 812m ( $v_{sym}CS_2^{-}$ ); 556m, 536m, 523s, 502sbr (R<sub>3</sub>P); 467m, 430br, 368m, 326br; 301m (Cu-N). ESIMS (major positive-ions, CH<sub>3</sub>OH), m/z (%): 676 (100) [{Cu[P(C\_6H\_5)\_2(2-C\_6H\_4COOH)]\_2}]^+. ESIMS (major negative-ions, CH<sub>3</sub>OH), m/z (%): 279 (20)  $[LCS_2]^-$ , 305 (100)  $[P(C_6H_5)_2(2-C_6H_4COOH)-H]^-$ , 674 (40)  $[{Cu[P(C_6H_5)_2(2-C_6H_4COOH)]_2-2H}]^-$ . Anal. Calc. for C<sub>31</sub>H<sub>30</sub>CuN<sub>4</sub>O<sub>2</sub>PS<sub>2</sub>: C, 57.35; H, 4.66; N, 8.63; S, 9.88. Found: C, 57.19; H, 4.54; N, 8.78; S, 10.02%.

# 2.1.4. [LCS<sub>2</sub>]Cu[PTA] (4)

To an acetonitrile solution (40 ml) of  $[Cu(CH_3CN)_4][PF_6]$ (0.373 g, 1.0 mmol) a methanol solution (10 ml) of 1,3,5-triaza-7-phosphaadamantane (PTA, 0.314 g, 2.0 mmol) was added at room temperature and the solution was stirred for 5 h. A methanol solution (10 ml) of Li[LCS<sub>2</sub>] (0.314 g, 1.0 mmol) was added and the reaction mixture was stirred for 3 h. The solvent was removed under vacuum, the resulting solid was treated with methanol/diethyl ether (50 ml) and salt removed by filtration. The solution was concentrated under vacuum and an orange solid was filtered off and recrystallized from methanol to give complex 4 in 78% yield. M.p. 237 °C dec. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 293 K):  $\delta$  2.23 (s, 6H,  $3-CH_3$ , 2.46 (s, 6H, 5-CH<sub>3</sub>), 4.26 (d, 6H, CH<sub>2</sub>), 4.62 (s, 6H, CH<sub>2</sub>), 5.92 (s, 2H, 4-CH), 7.47 (s, 1H, CHCS<sub>2</sub>). <sup>1</sup>H NMR (DMSO, 293 K): δ 2.18 (s, 6H, 3-CH<sub>3</sub>), 2.40 (s, 6H, 5-CH<sub>3</sub>), 4.19 (d, 6H, CH<sub>2</sub>), 4.50 (m, 6H, CH<sub>2</sub>), 6.10 (s, 2H, 4-CH), 7.28 (s, 1H, CHCS<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 293 K):  $\delta$  -90.19 (sbr). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 223 K):  $\delta$ -90.78 (sbr). IR (nujol, cm<sup>-1</sup>): 3126w, 3096w (CH); 1555s (C=N, C=C); 1095s, 1066s, 1040s (v<sub>asvm</sub>CS<sub>2</sub><sup>-</sup>); 880m, 851s, 812s (v<sub>sym</sub>CS<sub>2</sub><sup>-</sup>); 581s, 573s (R<sub>3</sub>P); 480m, 467m, 451m, 430m, 396m, 340w; 295mbr (Cu-N). ESIMS (major positive-ions, CH<sub>3</sub>OH), m/z (%): 501 (100) [{(LCS<sub>2</sub>)- $Cu[PTA] + H\}]^+$ , 523 (80) [{(LCS<sub>2</sub>)Cu[PTA] + Na}]^+, 687 (70)  $[\{(LCS_2)_2Cu_2 + H\}]^+$ . ESIMS (major negative-ions, CH<sub>3</sub>OH), m/z (%): 279 (100) [LCS<sub>2</sub>]<sup>-</sup>. Anal. Calc. for  $C_{18}H_{27}CuN_7PS_2$ : C, 43.23; H, 5.44; N, 19.61; S, 12.82. Found: C, 43.09; H, 5.41; N, 19.48; S, 12.66%.

#### 2.1.5. $[LCS_2]Cu[P(CH_2OH)_3]_2$ (5)

To a methanol/acetonitrile (1:2) solution (50 ml) of  $[Cu(CH_3CN)_4][PF_6]$  (0.373 g, 1.0 mmol) and  $P(CH_2OH)_3$ 

(0.248 g, 2.0 mmol), Li[LCS<sub>2</sub>] (0.286 g, 1.0 mmol) was added at room temperature. After addition, the reaction mixture was stirred for 6 h and solvent removed under vacuum. The resulting solid was treated with chloroform (50 ml) and salt removed by filtration. The solution was concentrated under vacuum and a brown solid was filtered off and re-crystallized from CHCl<sub>3</sub>/acetone (1:1) to give complex 5 in 81% yield. M.p. 222 °C dec. <sup>1</sup>H NMR (DMSO, 293 K):  $\delta$  2.23 (s, 6H, 3-CH<sub>3</sub>), 2.41 (s, 6H, 5-CH<sub>3</sub>), 4.00 (d, 12H, CH<sub>2</sub>), 6.07 (s, 2H, 4-CH), 7.30 (s, 1H, CHCS<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO, 293 K): δ 10.85 (5-CH<sub>3</sub>), 13.65 (3-CH<sub>3</sub>), 55.40 (CH<sub>2</sub>), 78.59 (CHCS<sub>2</sub>), 106.01 (4-CH), 140.37 (5-CCH<sub>3</sub>), 147.78 (3-CCH<sub>3</sub>).  $^{-31}P{^{1}H}$ NMR (DMSO, 293 K):  $\delta$  -8.20 (sbr). IR (nujol, cm<sup>-1</sup>): 3300br, 3180br (OH); 3060w (CH); 1555s (C=N, C=C); 1066m, 1038s, 1021s ( $v_{asym}CS_2^{-}$ ); 870s, 851s, 806m, 794s  $(v_{svm}CS_{2});$  547w, 503s  $(R_{3}P);$  465m, 453br, 431s, 396s, 341w, 321m; 296w (Cu-N). ESIMS (major positive-ions, CH<sub>3</sub>OH), m/z (%): 312 (100) {Cu[P(CH<sub>2</sub>OH)<sub>3</sub>]<sub>2</sub>}<sup>+</sup>. ESIMS (major negative-ions, CH<sub>3</sub>OH), m/z (%): 279 (100) [LCS<sub>2</sub>]<sup>-</sup>. Anal. Calc. for C<sub>18</sub>H<sub>33</sub>CuN<sub>4</sub>P<sub>2</sub>O<sub>6</sub>S<sub>2</sub>: C, 36.57; H, 5.63; N, 9.48; S, 10.85. Found: C, 36.29; H, 5.48; N, 9.28; S, 10.66%.

# 2.2. X-ray measurements and structure determination for complex 1

Crystal and experimental data are summarized in Table 1. Crystallization of compound  $[LCS_2]Cu[P(C_6H_5)_3]$ , 1, from chloroform/*n*-hexane solution, yields crystals suitable for the X-ray crystallography analysis performed on a XCS-Huber four-circle diffractometer (Department of Chemistry, University of Rome "La Sapienza") using zirconium-monochromatized Mo K $\alpha$  radiation (0.71073 Å). The cell parameters were refined by least square from the angular positions of 48 reflections in the range  $11.76^\circ < 2\theta < 27.13^\circ$ . The data were measured at room temperature for  $4.42^{\circ} < 2\theta < 59.94^{\circ}$ using a  $\theta/2\theta$  scan technique, and showed no decay. The data were processed to yield values of I and  $\sigma(I)$  corrected for Lorentz, polarization, and shape anisotropy effects. A total of 4133 independent reflections having  $F_0 > 3\sigma(F_0)$  were processed by the direct methods, which provided the complete structure. All non-hydrogen atoms were refined by a full-matrix least squares method with anisotropic thermal parameters. The hydrogen atoms were idealized (C-H = 0.96 Å; each of them was assigned 1.3 \* equiv. isotropic temperature factor of the parent atom and allowed to ride on it. The final difference Fourier map, with a rootmean-square deviation of electron density of  $0.06 \text{ e} \text{ \AA}^{-3}$ showed minimum and maximum values of -0.42 and 0.44, respectively. Calculations were performed using: xcs data collection program [38]; DARX2002 data reduction program [39]; "Il milione" structure determination and refinement package [40]; PLATON to prepare supplementary material [41]. The crystal structure is shown in Fig. 2 along with the atom-numbering scheme. The most interesting bond lengths and angles are presented in Table 2.

Table 1

С	rystal	data	and	structure	refinement	parameters	for [	LCS <sub>2</sub>	Cu[P(C	$C_6H_5)_3],$
1										

Molecular formula	$C_{30}H_{30}CuN_4PS_2$			
M	605.24			
Crystal size/mm	$(0.45 \times 0.25 \times 0.25)$			
Temperature (K)	293			
Wavelength (Å)	0.71073			
Crystal system	monoclinic			
Space group	$P2\overline{1}$			
a (Å)	13.067 (2)			
b (Å)	14.262 (2)			
<i>c</i> (Å)	17.121 (3)			
α (°)	90			
β (°)	112.21(2)			
γ (°)	90			
Volume (Å <sup>3</sup> )	2954.0(9)			
Ζ	4			
$D_{\rm c} ({\rm Mg}{\rm m}^{-3})$	1.361			
$\mu (\mathrm{mm}^{-1})$	0.961			
<i>F</i> (000)	1256			
Data collection range	$2.2^\circ <  heta < 30.0^\circ$			
Index ranges	$0 \leq h \leq 17; 0 \leq k \leq 19;$			
	$-22 \leqslant l \leqslant 21$			
Reflections collected	9229			
Independent reflections $[R_{int}]$	4499 [0.0091]			
Observed reflections	4133 [ $F > 3\sigma(F)$ ]			
Parameters refined	343			
a,b,c in the weighting scheme	0.5483, 0.0452, 0.0004			
$w = 1.0/(a + bF_{o} + cF_{o}^{2})$				
Final $R^{\rm a}$ indices	R = 0.029; wR = 0.040			
Goodness-of-fit, S <sup>b</sup>	0.95			
$(\Delta/\sigma)_{\rm max}$	0.06			
$\Delta \rho_{\rm max} \ ({\rm e} \ {\rm \AA}^{-3})$	0.44			
$\Delta \rho_{\min} (e \text{ Å}^{-3})$	-0.43			

<sup>a</sup> 
$$R = \sum ||F_o| - |F_c|| / \sum F_o; wR = \{\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2\}^{1/2}.$$
  
<sup>b</sup>  $S = \{\sum w(|F_o| - |F_c|)^2 / (N_{refl} - N_{param})\}^{1/2}.$ 

# 3. Results and discussion

## 3.1. Synthesis, properties and spectroscopic characterization

According to Eq. (1), 1:1:1 N-donor:copper:triorganophosphine Cu(I) complexes 1–4 have been obtained in high yields from the interaction of 1 equiv. of the lithium salt  $Li[LCS_2]$  with equimolar quantities of CuCl and tertiary monophosphines PR<sub>3</sub>, in a methanol/acetonitrile (1:2) solution at room temperature. The use of an excess of the phosphine did not change the stoichiometry of the resulting complexes.

$$Li[LCS_2] + CuCl + PR_3 \rightarrow [LCS_2]Cu[PR_3] + LiCl$$
(1)

1: 
$$PR_3 = P(C_6H_5)_3$$
  
2:  $PR_3 = P(C_6H_5)_2(4-C_6H_4COOH)$   
3:  $PR_3 = P(C_6H_5)_2(2-C_6H_4COOH)$   
4:  $PR_3 = PTA$ 

The reaction between Li[LCS<sub>2</sub>] and CuCl, carried in the presence of 2 equiv. of tris(hydroxymethyl)phosphine, under the conditions detailed above, yielded the mononuclear 1:1:2 N-donor:copper:triorganophosphine Cu(I) com-



Fig. 2. The molecular structure of complex 1. Ellipsoids are at the 30% probability level, and hydrogen atoms have been omitted for clarity.

Table 2 Selected geometries, [LCS<sub>2</sub>]Cu[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>], 1

Atoms	Parameter	Atoms	Parameter
Distances (Å)			
Cu1–S1	2.332(1)	N1-N2	1.362(4)
Cu1–P1	2.1851(8)	N1-C1	1.336(3)
Cu1–N1	2.089(2)	N2-C3	1.372(4)
Cu1–N3	2.080(2)	N2-C11	1.450(4)
S1-C12	1.687(3)	N3–N4	1.356(4)
S2-C12	1.658(3)	N3-C6	1.336(3)
P1-C13	1.832(3)	N4-C8	1.359(4)
P1-C19	1.828(3)	N4-C11	1.456(4)
P1-C25	1.830(3)	C11-C12	1.539(4)
Angles (°)			
Cu1-S1-C12	100.6(1)	S1-Cu1-N3	94.60(7)
N1-Cu1-N3	88.23(7)	S1-Cu1-P1	128.90(4)
N1–Cu1–P1	121.80(8)	S1-C12-C11	119.1(2)
N3–Cu1–P1	120.77(7)	S2-C12-S1	126.1(2)
S1-Cu1-N1	92.25(7)	S2-C12-C11	114.7(2)

plex 5 (Eq. (2)), likely due to the small sterical hindrance of the P(CH<sub>2</sub>OH)<sub>3</sub> phosphine.

$$Li[LCS_{2}] + CuCl + P(CH_{2}OH)_{3}$$
  

$$\rightarrow [LCS_{2}]Cu[P(CH_{2}OH)_{3}]_{2} + LiCl \qquad (2)$$

The stoichiometry of this compound was not affected by decreasing (1 equiv.) or increasing (>2 equiv.) the amount of  $P(CH_2OH)_3$ .

Compounds 1–4 are reasonably stable in air and show a good solubility in methanol, acetone, and chlorinated sol-

vents; derivative 5 is only soluble in DMSO. Derivatives 1-5 have been characterized by analytical and spectral data. The infrared spectra carried out on the solid samples (nuiol mull) showed all the bands required by the presence of the organic nitrogen and the phosphine ligands: weak absorptions in the range 3048-3126 cm<sup>-1</sup> are due to the azolyl ring C-H stretchings, and medium to strong absorptions near  $1555 \text{ cm}^{-1}$  are related to ring "breathing" vibrations. The presence of the  $CS_2$  moiety is detected by intense absorptions in the range  $1019-1099 \text{ cm}^{-1}$  and 791-880 $cm^{-1}$ , due to the asymmetric and symmetric  $CS_2^{-1}$  stretching modes, the shift with respect to free neutral ligand [35] being observed upon complex formation. These values fit those reported for analogous Ti(IV) [26,35], Zr(IV) [33], Hf(IV) [33], Y(III) and Sc(III) [21] complexes. In the far-IR spectra of derivatives 1-5, we have assigned the broad absorptions from 400 to  $550 \text{ cm}^{-1}$  to the phenyl quadrant in and out of plane bending vibrations, on the basis of previous reports on free phosphines [42], and copper(I)phosphine complexes [43]. In all the complexes weak to medium bands at *ca.*  $300 \text{ cm}^{-1}$  are observed; they are similar to those described for copper- and silver-azolato complexes [7,44], which have been tentatively assigned to v(M–N) stretching vibrations.

The room-temperature <sup>1</sup>H NMR spectra of derivatives 1-5 in CDCl<sub>3</sub> or DMSO solution (see Section 2), exhibit only one set of signals for the protons of the pyrazolyl rings of the  $[LCS_2]^-$  ligand, lightly shifted with respect to the same signals in the free ligand. This effect is particularly significant for the aliphatic CH signal of the CHCS<sub>2</sub><sup>-</sup> moiety in the <sup>1</sup>H NMR spectra of complexes 1–5 recorded in DMSO. The signals in the range 7.28–7.41 ppm were attributable to the CH aliphatic groups bound to the coordinated CS<sub>2</sub><sup>-</sup>, strongly deshielded with respect to the signal at  $\delta = 6.76$  ppm in the CHCS<sub>2</sub><sup>-</sup> moiety of the free ligand: this is in accordance with a  $\kappa^3$ -N,N,S coordination of the ligand in all the Cu(I) complexes. The tridentate coordination of the  $[LCS_2]^-$  ligand is confirmed by the  ${}^{13}C{}^{1}H$ NMR data. In particular for compounds 1 and 5 the signals at  $\delta = 79.36$  and 78.59 ppm, respectively, were assigned to the CHCS<sub>2</sub><sup>-</sup> moiety, while the signal at  $\delta = 87.19$  ppm corresponds to the CHCS<sub>2</sub><sup>-</sup> group in the free ligand. In the  ${}^{31}P{}^{1}H{}$  NMR spectra of complexes 1-3 only one broad peak is observed at 293 K and no significant variations are detected in the <sup>31</sup>P{<sup>1</sup>H} NMR profiles on lowering the temperature; at 223 K, the signals fall at 6.91, 7.16 and 0.91 ppm, in agreement with a CuP coordination core. The room temperature  ${}^{31}P{}^{1}H$  NMR spectrum of complex 4, in chloroform solution, exhibits a broadened signal centred at -90.19 ppm (at -90.78 in the spectrum recorded at 223 K). The room temperature <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of complex **5**, in DMSO solution, exhibits a broadened signal centred at -8.20 ppm, typical of a CuP<sub>2</sub> coordination core [45], significantly downfield shifted if compared to the signal at  $\delta$  –24.7 ppm exhibited by uncoordinated  $P(CH_2OH)_3$ . The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of derivatives 1-5 exhibit a broad singlet which, on addition of an excess of free phosphines, shifts upfield without observing a distinct resonance of the free phosphines; this is consistent with a fast exchange of coordinated and free phosphine ligands [46–48] and the <sup>31</sup>P–<sup>63/65</sup>Cu spin couplings (<sup>63</sup>Cu and <sup>65</sup>Cu, I = 3/2) are not observed.

Electrospray ionization mass spectroscopy was used to probe the existence of aggregates of the scorpionate ligand with Cu(I) and phosphine co-ligands in solution. Both positive-ion and negative-ion spectra of complexes 1-5, dissolved in methanol, were recorded at low voltage (3.5-4.0 kV); under these experimental conditions the dissociation is minimal and most of the analyte is transported to the mass spectrometer as the intact molecular species. The positive-ion spectra of compounds 1 and 2 were dominated by the fragments  $[{(LCS_2)Cu[P(C_6H_5)_3]_2 + Cu]}]^+$ m/z 931 (100%) and [{(LCS<sub>2</sub>)Cu[P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>at  $(4-C_6H_4COOH)_2 + Cu\}^+$  at m/z 1019 (100%), respectively; in the spectrum of derivative 2 we also observed a minor peak due to the protonated species  $[{(LCS_2)Cu[P(C_6H_5)_2 (4-C_6H_4COOH)$ ] + H}]<sup>+</sup>. Instead, in the positive-ion spectrum of compound 3 we observed the peak attributable to the fragment ion  $[{Cu[P(C_6H_5)_2(2-C_6H_4COOH)]_2}]^+$ , generated by the loss of the scorpionate ligand. The negative-ion spectra of compounds 1, 2 and 3 were dominated by the fragments due to the free scorpionate ligand  $[LCS_2]^-$ , or the related copper(I) aggregate  $[{(LCS_2)Cu + }$ Cl}]<sup>-</sup>. Only in the negative-ion spectrum of compound 3 we observed peaks attributable to the species  $[P(C_6H_5)_2(2-C_6H_4COOH)-H]^{-1}$ and  $[{Cu[P(C_6H_5)_2(2 C_6H_4COOH)_2-2H\}^-$ , generated by the loss of one or two protons of the phosphane ligand. In the positive-ion spectrum of compound 4 we observed the peaks due to the fragments  $[\{(LCS_2)Cu[PTA] + H\}]^+$  at m/z 501 (100%) and  $[\{(LCS_2)Cu[PTA] + Na\}]^+$  at m/z 523 (100%). The positive- and negative-ion spectrum of compound [LCS<sub>2</sub>]Cu[P(CH<sub>2</sub>OH)<sub>3</sub>]<sub>2</sub>, 5 were dominated by the fragments  $\{Cu[P(CH_2OH)_3]_2\}^+$  at m/z 312 (100%) and  $[LCS_2]^-$  at m/z 279 (100%), respectively.

## 3.2. X-ray crystallography

The monomeric complex 1 contains the tridentate heteroscorpionate ligand bonded to metal through the two nitrogen atoms from the pyrazolyl rings and the sulfur atom from the thioacetate group of the  $[LCS_2]^-$  ligand. The copper centre is in a tetrahedral environment with the P1 phosphorus atom from the triphenylphosphine coligand and the S1, N1, N3 atoms occupying the vertices. The Cu distances from the base planes of the tetrahedron are 0.659(2)Å (plane P1-N1-N3), 0.516(3) (plane S1-P1-N1), 0.497(2) (plane S1–P1–N3) and 1.210(2) Å (plane S1–N1–N3) showing a deviation from the ideal tetrahedral coordination. Furthermore, the angle between the plane (P1-N1-N3) and the Cu-S1 axis, 68.6(2)°, the plane (S1-P1-N1) and the Cu-N3 axis, 71.5(3)°, the plane (S1-P1-N3) and the Cu-N1 axis, 70.5(3)°, the plane (S1-N1-N3) and the Cu–P1 axis,  $82.3(2)^\circ$ , and the values of the angles

S–Cu–P, 128.90(4)°, and S–Cu–N, 92.25(7)° and 94.60(7)°, show the extent of distortion around the copper atom, due to the constraints imposed by the chelating ligand. The metal atom is displaced from the plane defined by the N1–N2–N3–N4 atoms by 0.978(2) Å. In addition the Cu atom is out of the pyrazolyl planes, defined by N1–N2–C1–C2–C3 and N3–N4–C6–C7–C8, at distances of 0.102(1) Å and 0.283(1) Å, respectively. The two pyrazolyl planes are planar within the limits of experimental values (max deviations are 0.002(3) Å and 0.009(2) Å, respectively) and the angle between them is 50.3(2)°.

The two Cu–N bond distances, 2.089(2) Å and 2.080(2) Å, are comparable with the values found in the complex of copper(I), HB- $(\mu$ -pz)<sub>3</sub>-Cu[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>], 2.081(5) Å and 2.065(5) Å [49] and HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>-Cu[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>], 2.10(1) Å and 2.09(1) Å [50]. The Cu-P bond distance 2.1851(8) Å lies at the lower limit of the range 2.15-2.30 Å reported for phosphine copper(I) complexes [50], but is significantly longer than the values 2.153(2) Å [49] and 2.166(6) A [50]. The Cu–S1 bond distance, 2.332(1) Å, is significantly shorter than the values observed in complexes containing  $Cu^{I}$ -S-C(=S)R moieties such as 2.395(1), 2.429(1) Å [51] and 2.431(1), 2.456(1) Å [52]. Even if the C12–S1, 1.687(3) Å, is slightly longer than C12–S2, 1.658(3) Å, they fall in the lower end of the normal range observed in similar compounds, 1.64–1.79 Å [53]. This seems to indicate the existence of a delocalized S-C-S bond in the complex.

The intraligand N3–Cu–N1, N3–Cu–S1, N1–Cu–S1 angles are restrained by the chelate rings to 88.23(7), 94.60(7) and 92.25(7)°. The values of distances and angles around the copper atom are comparable to those previously reported in analogous phosphine copper(I) derivatives of tris(pyrazolyl)methanesulfonate ligand (Tpms) coordinated to copper(I) in the  $\kappa^3$ -N,N',O fashion [54], and in (unidentate phosphine)(bidentate pyrazolate)metal(I) arrays of the type [Tp]M<sup>I</sup>(R<sub>3</sub>P)<sub>n</sub> (M<sup>I</sup> = Cu<sup>I</sup> or Ag<sup>I</sup>; n = 1 or 2; Tp = bis- or tetrakis-(pyrazolyl)borate) [55].

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#### Appendix A. Supplementary material

CCDC 644148 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.09.017.

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