



Hypodentate coordination of *N,N*-di(alkyl/aryl)-*N'*-acylthiourea derivatives in Cu(I) complexes

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ABSTRACT

New four-coordinated tetrahedral Cu(I) complexes of the general formula [CuCl(HL)(PPh₃)₂] have been synthesized from the reactions between [CuCl₂(PPh₃)₂] and *N*-(dibenzylcarbamothioyl)benzamide (HL1) or *N*-(methylpentylcarbamothioyl)benzamide (HL2) in benzene. The complexes have been characterized by elemental analyses, IR, UV–Vis, ¹H, ¹³C and ³¹P NMR spectroscopy. The molecular structures of [CuCl(HL1)(PPh₃)₂] (**1**) and [CuCl(HL2)(PPh₃)₂] (**2**) were determined by single crystal X-ray crystallography. Each complex displays a distorted tetrahedral, ClP₂S, coordination geometry with hypodentate coordination of acylthiourea ligands which coordinate the Cu(I) centre through sulfur atom exclusively.

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1. Introduction

Generally, a reaction between a transition metal ion and a multidentate ligand proceeds with coordination of all suitably disposed ligand donor atoms to form a metal complex with concomitant formation of chelate ring(s). One reason for this might be the entropy increase which occurs on replacement of monodentate ligands of the metal precursor by the donor atoms of a multidentate ligand to form chelate rings [1]. However, there are some examples in which multidentate ligands are coordinated through less than maximum number of potential donor atoms and avoid the formation of chelate ring(s) [2]. Constable has introduced the term 'hypodentate' to describe this type of coordination [3]. Metal complexes of hypodentate ligands have gained importance in the view of design and syntheses of heteropolymetallic systems [4,5].

N-Alkyl/aryl-*N'*-acylthiourea or *N,N*-di(alkyl/aryl)-*N'*-acylthiourea are known to form stable complexes with a large number of transition metal ions [6–8]. Due to the presence of O, N, N' and S donor atoms, these versatile ligands coordinate in four different modes to the metal ions. In the majority of their structurally characterized complexes, they act as chelating bidentate O,S-monoanionic ligands [9,10]. Hypodentate coordination only through sulfur as neutral, monodentate ligand is rare and seen in some Au(I) [11], Ag(I) [12], Hg(II) [13], Pt(II) [14,15] and Cu(I) [16,17] complexes. Examples of transition metal complexes with acylthiourea ligands as neutral

bidentate [18] or monobasic bridging ligands [19] are also rare. These thiourea derivatives exhibit remarkable applications in analytical and biological sciences [20–22]. The recent increase in attention paid to these complexes has arisen mainly due to their coordination versatility and varied applications such as in precious metal separation and extraction [20], single source precursors for nanomaterials [21], biological activity [23,24], etc. We have reported *N*-[di(alkyl/aryl)carbamothioyl]benzamide complexes of Ru(II) [25], Ru(III) [26], Cu(I) [27] and Co(III) [28] as catalysts for oxidation of alcohols to the corresponding carbonyl compounds in the presence of oxidants such as *N*-methylmorpholine-*N*-oxide (NMO)/hydrogen peroxide/*tert*-butyl hydroperoxide (TBHP). We report herein the synthesis, characterization and crystal structures of new four-coordinated tetrahedral copper(I) complexes containing hypodentate *N*-[(dibenzyl/methylpentyl)carbamothioyl]benzamide and triphenylphosphine ligands; see Fig. 1 for the chemical structures of the ligands used in this study.

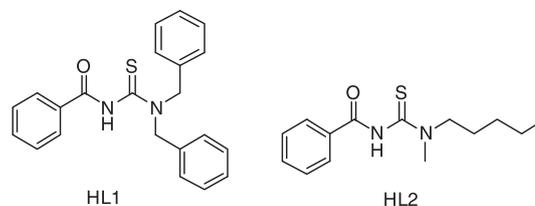


Fig. 1. Chemical structures of ligands investigated herein.

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2. Experimental

2.1. Materials and reagents

All the chemicals were obtained from commercial sources and used as received. The solvents were purified and dried in accordance with the standard literature methods. The precursor $[\text{CuCl}_2(\text{PPh}_3)_2]$ was prepared by the literature procedure [29]. *N*-(Benzylcarbamothioyl)benzamide (HL1) and *N*-(methylpentylcarbamothioyl)benzamide (HL2) were prepared from benzoyl chloride, potassium thiocyanate and dibenzyl amine or *n*-methylpentyl amine in dry acetone [30].

2.2. Physical measurements

Microanalyses were carried out with a Vario EL AMX-400 elemental analyzer. Melting points were recorded with a Veego VMP-D melting point apparatus and were uncorrected. FT-IR spectra were recorded as KBr pellets with a PerkinElmer Spectrum RX1 FT-IR spectrophotometer in the range 4000–400 cm^{-1} . Electronic spectra of the complexes were recorded in ethanol solutions using a PG Instruments Ltd T90+ spectrophotometer in the 800–200 nm range. Magnetic susceptibility measurements were made with a Sherwood Scientific auto magnetic susceptibility balance. ^1H , ^{13}C and ^{31}P NMR spectra were recorded in Bruker Avance 400 MHz instrument in CDCl_3 . TMS was used as an internal standard for ^1H and ^{13}C NMR spectra. H_3PO_4 was used as an internal standard for ^{31}P NMR spectra.

2.3. Synthesis of Cu(I) complexes

Both the complexes were prepared using the following general procedure. Ligand (HL) (0.1980–0.2703 g, 0.75 mmol) dissolved in benzene (15 mL) was added to $[\text{CuCl}_2(\text{PPh}_3)_2]$ (0.5 g, 0.75 mmol) in benzene (25 mL). The mixture was stirred for 36 h at 27 °C. This was concentrated to 3 mL and an ethyl acetate/*n*-hexane mixture (25 mL; 1:9) was added. The resultant orange oily precipitate was stirred, filtered, recrystallized from dichloromethane/*n*-hexane and dried *in vacuo*.

$[\text{CuCl}(\text{HL1})(\text{PPh}_3)_2]$ (**1**) was prepared from *N*-(dibenzylcarbamothioyl)benzamide (HL1) (0.2703 g, 0.75 mmol) and $[\text{CuCl}_2(\text{PPh}_3)_2]$ (0.5 g, 0.75 mmol). Single crystals suitable for X-ray diffraction were grown at room temperature from ethyl acetate. Yield: 88%, decomposition point 172 °C. *Anal. Calc.* for $\text{C}_{58}\text{H}_{50}\text{ClCuN}_2\text{OP}_2\text{S}$ (formula weight 984.04): C, 70.79; H, 5.12; N, 2.85; S, 3.26. Found: C, 70.76; H, 5.07; N, 2.78; S, 3.21%. $\mu_{\text{eff}} = 0$. FT-IR (KBr) ν cm^{-1} : 3329 (N–H), 1689 (C=O), 1255 (C=S), 1435, 1095, 744 (PPh_3). UV [ethanol, δ in nm (ϵ in $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 209 (68,142), 277 (20,828)]. ^1H NMR in CDCl_3 , δ ppm: 7.15–8.26 (m, 45H, aromatic), 11.80 (s, 1H, N–H), 4.68 (2H, CH_2), 5.13 (2H, CH_2). ^{13}C NMR in CDCl_3 , δ ppm: 175.50 (C=S), 158.45 (C=O), 121.96, 122.05, 123.19, 127.32, 127.47 (aromatic). ^{31}P NMR in CDCl_3 , δ ppm: 28.10 (s).

$[\text{CuCl}(\text{HL2})(\text{PPh}_3)_2]$ (**2**) was prepared from *N*-(methylpentylcarbamothioyl)benzamide (HL2) (0.1980 g, 0.75 mmol) and $[\text{CuCl}_2(\text{PPh}_3)_2]$ (0.5 g, 0.75 mmol). Single crystals suitable for X-ray diffraction were grown at room temperature from dichloromethane solution by the diffusion of diethyl ether vapour. Yield: 85%, decomposition point 165 °C. *Anal. Calc.* for $\text{C}_{50}\text{H}_{50}\text{ClCuN}_2\text{OP}_2\text{S}$ (formula weight 887.95): C, 67.63; H, 5.68; N, 3.15; S, 3.61. Found: C, 67.60; H, 5.63; N, 3.10; S, 3.58%. $\mu_{\text{eff}} = 0$. FT-IR (KBr) ν cm^{-1} : 3181 (N–H), 1690 (C=O), 1178 (C=S), 1435, 1094, 744 (PPh_3). UV [ethanol, λ in nm (ϵ in $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 209 (64,285), 270 (11,228)]. ^1H NMR in CDCl_3 , δ ppm: 7.27–8.19 (m, 35H, aromatic), 11.35 (s, 1H, N–H), 3.50 (t, 2H, CH_2), 3.18 (s, 3H, CH_3), 1.98–2.16 (m, 2H, CH_2), 1.69–1.78 (m, 2H, CH_2), 1.22–1.43 (m, 2H, CH_2), 0.92 (t, 3H, CH_3).

^{13}C NMR in CDCl_3 , δ ppm: 172.96 (C=S), 157.80 (C=O), 122.22, 123.47, 125.66, 125.77, 127.53, 127.67 (aromatic), 49.95, 35.25, 22.22, 19.31 (CH_2), 15.94, 7.66 (CH_3). ^{31}P NMR in CDCl_3 , δ ppm: 29.38 (s).

2.4. X-ray crystallography

Intensity data were measured at 100 K on an Agilent Technologies SuperNova Dual CCD with an Atlas detector fitted with Mo $K\alpha$ radiation with $\theta_{\text{max}} = 27.5^\circ$. The data processing and absorption correction were accomplished with CRYSLIS PRO [31]. The structures were solved by direct-methods with SHELXS-97 [32] and refinement (anisotropic displacement parameters, hydrogen atoms in the riding model approximation and a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ for $P = (F_o^2 + 2F_c^2)/3$) was on F^2 by means of SHELXL-97 [32]. The crystallographic data and the final refinement details are given in Table 1. Figs. 2 and 3 were drawn with ORTEP [33] at the 50% probability level and the remaining crystallographic figures were drawn with DIAMOND using arbitrary

Table 1
Crystal data for **1** and **2**.

Crystal data	1	2
Empirical formula	$\text{C}_{58}\text{H}_{50}\text{ClCuN}_2\text{OP}_2\text{S}$	$\text{C}_{50}\text{H}_{50}\text{ClCuN}_2\text{OP}_2\text{S}$
Formula weight	983.99	887.91
Crystal colour	light-yellow	colourless
Crystal dimensions (mm)	0.20 × 0.25 × 0.30	0.20 × 0.30 × 0.40
Crystal system	monoclinic	triclinic
Space group	$C2/c$	$P\bar{1}$
<i>a</i> (Å)	35.2407(11)	12.8918(4)
<i>b</i> (Å)	11.4936(3)	13.3376(5)
<i>c</i> (Å)	27.3488(9)	14.0061(5)
α (°)	90	100.287(3)
β (°)	118.896(4)	103.483(3)
γ (°)	90	104.271(3)
<i>V</i> (Å ³)	9698.3(5)	2197.29(13)
<i>Z</i>	8	2
<i>D</i> _{calc} (g cm ⁻³)	1.348	1.342
<i>F</i> (000)	4096	928
μ (Mo $K\alpha$) (mm ⁻¹)	0.658	0.718
Reflections collected	24 116	17 607
<i>R</i> _{int}	0.031	0.030
Unique reflections	10 824	9718
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	8906	8218
<i>R</i> [observed reflections]	0.037	0.037
<i>a</i> , <i>b</i> , in weighting scheme	0.043, 9.326	0.032, 1.047
<i>wR</i> (all data)	0.098	0.088

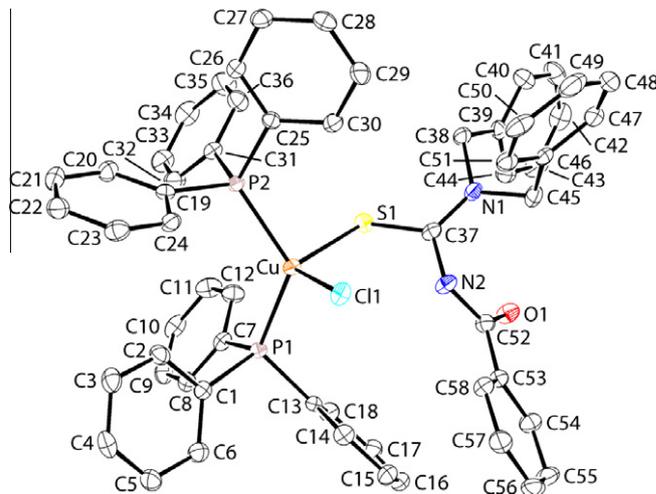


Fig. 2. Molecular structure of **1** showing atomic labelling schemes. The H atoms have been omitted for reasons of clarity.

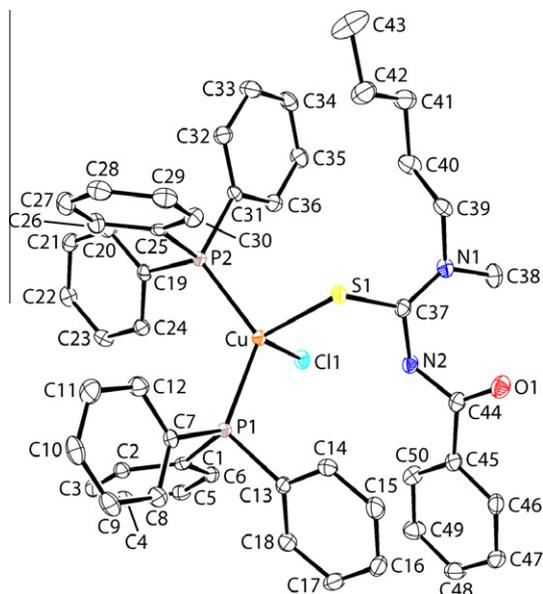


Fig. 3. Molecular structure of **2** showing atomic labelling schemes. The H atoms have been omitted for reasons of clarity.

spheres [34]. The data manipulation and the interpretation were done with WINGX [35] and PLATON [36].

3. Results and discussion

3.1. Synthesis

The Cu(I) complexes $[\text{CuCl}(\text{HL1})(\text{PPh}_3)_2]$ (**1**) and $[\text{CuCl}(\text{HL2})(\text{PPh}_3)_2]$ (**2**) reported here have been synthesized by reacting $[\text{CuCl}_2(\text{PPh}_3)_2]$ with *N*-(dibenzylcarbamothioyl)benzamide (HL1) or *N*-(methylpentylcarbamothioyl)benzamide (HL2), respectively, in benzene (Scheme 1), indicating that Cu(II) is reduced to Cu(I) during the course of reaction. Analytical, spectral and single crystal X-ray diffraction studies reveal that complexes **1** and **2** contain one molecule of HL1 and HL2, respectively, in addition to two molecules of PPh_3 . The HL1 and HL2 ligands exhibit neutral monodentate (hypodentate) coordination through the sulfur atom to Cu(I). The complexes obtained are orange, air-stable, non-hygroscopic in nature, soluble in acetone, acetonitrile, benzene, dichloromethane, chloroform, DMSO and DMF, and insoluble in *n*-hexane and water. The analytical data obtained are in good agreement with the proposed molecular formulae.

3.2. Spectroscopy

A medium intensity band was observed around $1239\text{--}1314\text{ cm}^{-1}$ in the FT-IR spectra of the free ligands which is characteristic of the

Table 2
Selected bond lengths (Å) and bond angles (°) for **1** and **2**.

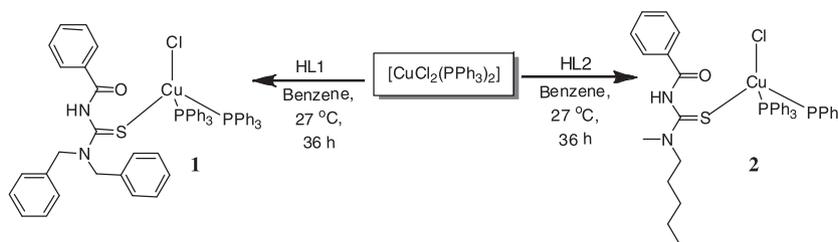
Parameter	1	2
Cu–Cl1	2.3322(5)	2.3430(5)
Cu–S1	2.3873(6)	2.3902(5)
Cu–P1	2.2718(5)	2.2745(5)
Cu–P2	2.2738(5)	2.2670(5)
S1–C37	1.688(2)	1.6920(19)
O1–C52	1.218(2)	1.221(2) ^a
N1–C37	1.325(3)	1.318(3)
N2–C37	1.408(2)	1.406(2)
Cl1–Cu–S1	106.434(19)	104.841(18)
Cl1–Cu–P1	107.71(2)	102.056(19)
Cl1–Cu–P2	108.54(2)	107.62(2)
S1–Cu–P1	110.95(2)	116.52(2)
S1–Cu–P2	96.71(2)	101.636(19)
P1–Cu–P2	124.91(2)	122.76(2)

^a Distance is for O1–C44.

C=S group [30]. In the spectra of complexes **1** and **2**, this band was observed in the lower frequency region, i.e. $1178\text{--}1255\text{ cm}^{-1}$, consistent with reduced electron density in this bond and therefore, suggesting the coordination of the sulfur atom to copper ion [37]. The free ligands exhibited a strong band corresponding to the C=O group in the region $1651\text{--}1693\text{ cm}^{-1}$ and to the N–H group in the region $3329\text{--}3181\text{ cm}^{-1}$ [38,39]. These bands also appeared in the same regions in the complexes, which indicate that, the C=O and N–H groups are in similar environments to those found in the uncoordinated ligands. In addition, the complexes showed new bands around 1435 , 1100 and 750 cm^{-1} , which are due to triphenylphosphine ligand [37].

The new copper complexes **1** and **2** were diamagnetic ($\mu_{\text{eff}} = 0$), indicating the presence of copper in the +1 oxidation state. In the UV–Vis spectra of complexes in ethanol solution, bands observed in the region $209\text{--}277\text{ nm}$ ($\epsilon = 11,228\text{--}68,142\text{ mol}^{-1}\text{ cm}^{-1}\text{ dm}^3$) have been assigned to metal to ligand charge transfer (MLCT) or ligand centred $\pi\text{--}\pi^*$ transitions [40].

The ^1H , ^{13}C and ^{31}P NMR spectra of **1** and **2** have been recorded in CDCl_3 solution. The ^1H NMR spectra showed a complex multiplet around $7.15\text{--}8.26\text{ ppm}$, which has been attributed to the aromatic protons present in the triphenylphosphine and *N*-[(dibenzyl/methylpentyl)carbamothioyl]benzamide ligands. The characteristic N–H signal in the region $11.35\text{--}11.80\text{ ppm}$ in the ligands was present in the ^1H NMR spectra of both the complexes indicating the non-participation of the N–H group in coordination. Complex **1** showed two singlets at 4.68 and 5.13 ppm , which are assigned to the methylene protons of the *N*-(dibenzylcarbamothioyl)benzamide ligand. In complex **1**, the amidic (O)C–NH and thioamidic NH–C(S), and (S)C–N(R/R) bonds of the coordinated ligand are shorter than the actual C–N single bond. Because of this partial double bond character of the (S)C–N(R/R) bond, the rotation around this bond is restricted in solution on the NMR time scale. Hence separated two singlets were observed for the two methylene groups of the (S)C–N(CH₂)₂– moiety in complex **1** [6]. The



Scheme 1. Synthesis of Cu(I) complexes **1** and **2**.

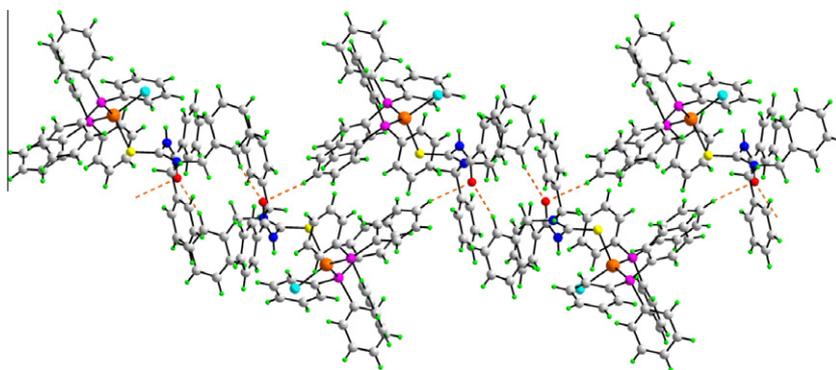


Fig. 4. Supramolecular chain in the crystal structure of **1**. The C–H...O and C–H...Cl interactions are shown as orange and blue dashed lines, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

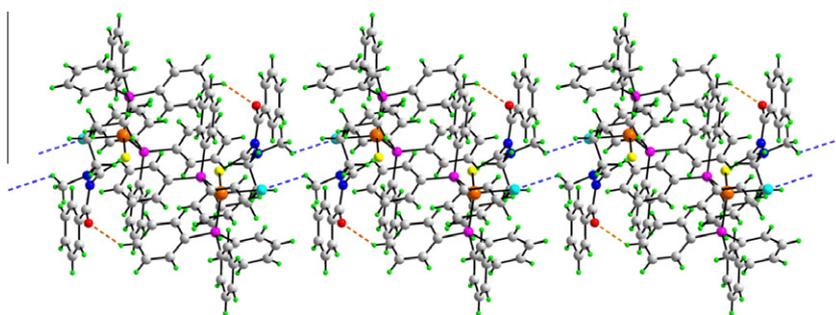


Fig. 5. Supramolecular chain in the crystal structure of **2**. The C–H...O and C–H...Cl interactions are shown as orange and blue dashed lines, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

same trend was also noted in the ^1H NMR spectrum of ligand HL1. A triplet appeared at 3.50 ppm in complex **2** due to the methylene protons proximate to nitrogen. Complex **2** also exhibited three multiplets at 1.98–2.16, 1.69–1.78 and 1.22–1.43 ppm which were attributed to remaining methylene protons of aliphatic carbon chain. A triplet at 0.92 ppm and a singlet at 3.18 ppm in complex **2** have been assigned to the terminal methyl protons of *N*-(methylpentylcarbamothioyl)benzamide ligand. The signals observed in the range 121.96–127.67 ppm in ^{13}C NMR spectra of **1** and **2** are attributed to the aromatic carbons present in the triphenylphosphine and *N*-[(dibenzyl/methylpentyl)carbamothioyl]benzamide ligands. The ^{13}C NMR spectra of both complexes showed signals in the region 172.96–175.50 and 157.80–158.45 ppm, which are assigned to the C=S and C=O carbons, respectively. Both the complexes exhibited resonances due to aliphatic carbons in the expected regions. Complexes **1** and **2** showed only one signal at 28.10 and 29.38 ppm, respectively in their ^{31}P NMR spectra.

3.3. Crystallography

The molecular structures of **1** and **2** are illustrated in Figs. 2 and 3, respectively, and selected geometric parameters are collected in Table 2. In **1**, the Cu(I) atom is coordinated by two phosphorus atoms of the phosphine ligands, a chloride atom and the sulfur atom derived from the *N*-(dibenzylcarbamothioyl)benzamide ligand (HL1). The coordination geometry is based on a tetrahedral geometry with the range of tetrahedral angles being a narrow $96.71(2)^\circ$ for S1–Cu–P2 to a wide $124.91(2)^\circ$ for P1–Cu–P2, i.e. as expected for the presence of two bulky phosphine ligands in the coordination sphere. Of particular interest is the monodentate mode of coordination for the HL1 ligand. The carbonyl-O1 atom is directed away

from the Cu(I) centre and the amine-H participates in an intramolecular N–H...Cl hydrogen bond to close a $S(6)\{\dots\text{HNCSCuCl}\}$ ring.¹ Moreover, a comparison of the S–C and N–C parameters in the uncoordinated ligand, HL1 [38], with those in **1** confirm little change in the electronic structures. For example, the C=S bond in **1** of 1.688(2) Å is equal within experimental error compared to the equivalent bond in HL1 of 1.676(3) and 1.678(3) Å for the two independent molecules comprising the asymmetric unit [38].

The molecular structure of **2** closely resembles that of **1** with the comparable bond distances for the complexes being equal or approximately equal. The main difference between **1** and **2** is the narrower range of tetrahedral angles in **2**, Table 2. There is a comparable disposition of the potential donor atoms of the HL2 molecule in **2**, as for HL1 in **1**, and the intramolecular N–H...Cl hydrogen bond persists.¹ Finally, the experimental equivalence between the key geometric parameters involving the potential donor atoms in **2** with those in the structure of the uncoordinated ligand, HL2 [39] is noted.

There is only one crystal structure in the literature where *N*-[di(alkyl/aryl)carbamothioyl]benzamide molecules coordinate in a monodentate fashion to Cu(I), namely, in the structure of $[\text{Cu}(\text{HL})_3\text{Cl}]$, [HL = $\text{Et}_2\text{NC}(=\text{S})\text{N}(\text{H})\text{C}(=\text{O})\text{C}_6\text{H}_4\text{-p}$], where three HL molecules each coordinate the Cu(I) atom via the sulfur atom only [41].

In the crystal structure of **1**, the most prominent intermolecular interactions are of the type C–H...O whereby the carbonyl-O1 atom

¹ Intramolecular N2–H...Cl1 interaction operating in the crystal structures of **1** and **2**. $[\text{Cu}(\text{HL1})(\text{PPh}_3)_2]$ (**1**): N2–H2...Cl1 = 2.35 Å, N2...Cl1 = 3.1362(18) Å, and angle at H2 = 150° . $[\text{Cu}(\text{HL2})(\text{PPh}_3)_2]$ (**2**): N2–H2...Cl1 = 2.31 Å, N2...Cl1 = 3.1080(19) Å, and angle at H2 = 152° .

is bifurcated.² These interactions assemble molecules into supramolecular chains along [101], Fig. 4. Molecules are consolidated in the three-dimensional crystal structure by C–H... π interactions.² A supramolecular chain is also featured in the crystal structure of **2**. Here, centrosymmetrically related molecules are connected via C–H...O contacts and these are linked into a chain along [001] via C–H...Cl contacts [41], Fig. 5. Again, as for **1**, C–H... π interactions consolidate the crystal packing in **2**.²

4. Conclusions

The present study shows synthesis and full characterization of new four-coordinated tetrahedral copper(I) complexes containing *N*-[(dibenzyl/methylpentyl)carbamothioyl]benzamide and triphenylphosphine ligands. *N*-[(Dibenzyl/methylpentyl)carbamothioyl]benzamide exhibit rare examples of neutral monodentate (hypodentate) coordination through sulfur to copper.

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Appendix A. Supplementary data

CCDC 845840 and 845841 contain the supplementary crystallographic data for compounds **1** and **2**, respectively. 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.

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² Intermolecular interactions operating in the crystal structures of **1** and **2**. [CuCl(HL1)(PPh₃)₂] (**1**): C47–H47...O1ⁱ = 2.38 Å, C47...O1ⁱ = 3.300(3) Å, and angle at H47 = 162° for symmetry operation (i): 3/2 – x, 1/2 – y, 1 – z. C10–H10...O1ⁱⁱ = 2.59 Å, C10...O1ⁱⁱ = 3.506(3) Å, and angle at H10 = 163° for symmetry operation (ii): 1 – x, y, 1/2 – z. Shortest C–H... π interaction: C41–H41...Cg(C53–C58)ⁱ = 2.77 Å, C41...Cg(C53–C58)ⁱ = 3.513(3) Å, and angle at H2a = 136°. [CuCl(HL2)(PPh₃)₂] (**2**): C28–H28...O1ⁱ = 2.44 Å, C28...O1ⁱ = 3.249(3) Å, and angle at H28 = 142° for symmetry operation (i): 1 – x, –y, 1 – z. C38–H38b...Cl1ⁱⁱ = 2.44 Å, C38...Cl1ⁱⁱ = 3.249(3) Å, and angle at H38b = 123° for symmetry operation (ii): 1 – x, –y, –z. Shortest C–H... π interaction: C10–H10...Cg(C19–C24)ⁱⁱⁱ = 2.68 Å, C10...Cg(C19–C24)ⁱⁱⁱ = 3.596(2) Å, and angle at H10 = 163° for symmetry operation (iii): 1 – x, 1 – y, –z.