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Polyhedron 27 (2008) 175–180
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Three- and four-coordinate copper(I) halide complexes of 2-(diphenylphosphano)benzaldehyde: Dimerization induced by thione-S ligation

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Received 14 June 2007; accepted 5 September 2007
Available online 1 November 2007

Abstract

Reactions of copper(I) halides with 2-(diphenylphosphano)benzaldehyde (PCHO) in 1:2 molar ratio afforded mononuclear complexes of the type $[CuX(PCHO)_2]$, whereas treatment of these compounds with equimolar amounts of pyridine-2-thione or pyrimidine-2-thione gave rise to the formation of mixed-ligand dimers of the formula $[CuX(PCHO)(thione)]_2$. The molecular structures of $[CuCl(PCHO)_2]$, $[CuBr(PCHO)_2]$ and $[CuCl(PCHO)(pymtH)]_2$ have been established by single-crystal X-ray diffraction. The two homoleptic complexes feature a trigonal copper(I) centre with the phosphane acting as a monodentate ligand via the P atom. In the structure of the dimeric mixed-ligand complex each of the two metal centres exhibit a distorted tetrahedral environment with the thione-S atoms acting in a doubly bridging mode.

Keywords: Copper(I) halide complexes; 2-(Diphenylphosphano)benzaldehyde; Heterocyclic thiones; Structures

1. Introduction

There is much current interest in copper(I) coordination chemistry, mainly because of its participation in certain biochemical redox reactions [1]. Due to the favorable soft acid–soft base interaction, the chemistry of this closed-shell d^{10} metal ion is largely based upon coordination to ligands containing phosphorus and sulfur donor atoms. Thus, with tertiary phosphanes, copper(I) produces a vast number of complexes which feature an extraordinary stoichiometric and geometrical variety. Many of these complexes have been intensively employed in catalytic processes [2] and some of them were even found to exhibit antitumor activity [3]. As far as the sulfur containing ligands are concerned, heterocyclic thioamides represent a class of compounds that have attracted substantial interest over the last few decades, largely because of their relevance to biological systems [4,5].

Based on the rich chemistry so far found for each of the two aforementioned classes of ligands, we have been interested in examining univalent copper and silver mixed-ligand complexes bearing both neutral heterocyclic thiones and bulky triaryl phosphane ligands with respect to the factors that influence the structural characteristics of these compounds [6,7]. Since our findings showed the coordination number to be related to the steric requirements on the part of the phosphane ligand only [8], we recently focused on phosphanes that may introduce imposed steric effects around the metal centre. In the present work we report on the synthesis and characterization of some Cu^I complexes derived from 2-(diphenylphosphano)benzaldehyde (PCHO). Apart from its steric demands, the selection of PCHO as ligand is further based on its salient feature to bear, besides the “soft” phosphorus donor, a “hard” oxygen atom, thus being capable of behaving as a P,O-chelate [9].

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doi:10.1016/j.poly.2007.09.001

2. Experimental

2.1. Materials and instrumentation

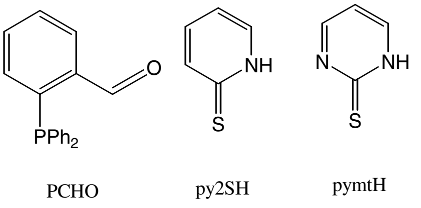
Commercially available copper(I) halides and 2-(diphenylphosphano)benzaldehyde (Aldrich) were used as received while the thiones (Merck) were re-crystallized from hot ethanol prior to their use (Scheme 1). All the solvents were purified by respective suitable methods and allowed to stand over molecular sieves. Infra-red spectra in the region of 4000–250 cm^{-1} were obtained in KBr discs with Perkin–Elmer FT-IR Spectrum 1 spectrophotometer, while a Perkin–Elmer-Hitachi 200 spectrophotometer was used to obtain the electronic absorption spectra. ^{1}H NMR spectra were recorded on a Brucker AM 300 spectrometer at 298 K with positive chemical shifts given downfield from internal TMS. Melting points were measured in open tubes with a STUART scientific instrument and are uncorrected.

2.2. Crystal structure determination

Single crystals suitable for crystal structure analysis were obtained by slow evaporation of acetonitrile/methanol solutions of the complexes at room temperature. X-ray diffraction data were collected on an Enraf-Nonius Kappa CCD area-detector diffractometer. The programs DENZO [10] and COLLECT [11] were used in data collection and cell refinement. Details of crystal and structure refinement are shown in Table 1. The structures were solved using program SIR97 [12] and refined with program SHELX-97 [13]. Molecular plots were obtained with program ORTEP-3 [14].

2.3. Synthesis of complexes **1–3**

A suspension of 0.25 mmol of copper(I) halide (24.75 mg for CuCl, 35.85.7 mg for CuBr, 47.6 mg for CuI) in 30 cm^3 of dry acetonitrile was stirred at 50 °C until a clear yellow solution was formed. To this, a solution of 145 mg (0.5 mmol) of 2-(diphenylphosphano)benzaldehyde in 25 cm^3 of dry acetonitrile was added and the mixture was stirred for 2 h at 50 °C. The resulting bright yellow solution was filtered off and left to evaporate at ambient. The microcrystalline solid, which was deposited upon standing for several days, was filtered off and dried *in vacuo*.



Scheme 1. The phosphane and the heterocyclic thiones used as ligands with their abbreviations.

2.3.1. [CuCl(PCHO)$_2$] (**1**)

Orange crystals (21 mg, 12%), m.p. 232 °C; *Anal.* Calc. for $C_{38}H_{30}ClCuO_2P_2$: C, 67.16; H, 4.45. Found: C, 67.24; H, 4.58%. IR (cm^{-1}): 3054m, 2824w, 2761m, 1696vs, 1668vs, 1583m, 1561m, 1481s, 1392m, 1295m, 1200vs, 1096s, 864m, 764m, 748vs, 696vs, 527vs, 508vs, 462s. ^{1}H NMR (CDCl$_3$, δ ppm): 9.98 (s, 1H, –CHO), 7.83 (d, 1H, $J_{H–H} = 7.3$ Hz, H^3–PhCHO), 7.58 (t, 1H, $J_{H–H} = 7.3$ Hz, H^5–PhCHO), 7.49 (t, 1H, $J_{H–H} = 7.3$ Hz, H^4–PhCHO), 7.40 (m, 4H, Ph, H^{2,6}), 7.26 (m, 6H, Ph, H^{2,6}), 6.99 (d, $J_{H–H} = 7.3$ Hz, H^6-PhCHO).

2.3.2. [CuBr(PCHO)$_2$] (**2**)

Orange crystals (45 mg, 24%), m.p. 230 °C; *Anal.* Calc. for $C_{38}H_{30}BrCuO_2P_2$: C, 63.04; H, 4.18. Found: C, 62.98; H, 4.25%. IR (cm^{-1}): 3061m, 2839m, 2745m, 1697s, 1676vs, 1560s, 1479s, 1435vs, 1393m, 1294s, 1203vs, 1094s, 1091vs, 846vs, 760vs, 749vs, 703vs, 691vs, 676s, 529vs, 509vs, 462s. ^{1}H NMR (CDCl$_3$, δ ppm): 9.95 (s, 1H, –CHO), 7.84 (d, 1H, $J_{H–H} = 7.3$ Hz, H^3–PhCHO), 7.58 (t, 1H, $J_{H–H} = 7.3$ Hz, H^5–PhCHO), 7.50 (t, 1H, $J_{H–H} = 7.3$ Hz, H^4–PhCHO), 7.40 (m, 4H, Ph, H^{2,6}), 7.26 (m, 6H, Ph, H^{2,6}), 6.99 (d, $J_{H–H} = 7.3$ Hz, H^6-PhCHO).

2.3.3. [CuI(PCHO)$_2$] (**3**)

Yellow crystals (33 mg, 17%), m.p. 241 °C; *Anal.* Calc. for $C_{38}H_{30}ClCuO_2P_2$: C, 59.19; H, 3.92. Found: C, 60.09; H, 4.01%. IR (cm^{-1}): 3058m, 2839m, 2744m, 1697s, 1675vs, 1560m, 1479s, 1435vs, 1385m, 1294s, 1203vs, 1094m, 1091s, 847s, 759vs, 744s, 703s, 691vs, 677s, 529vs, 509vs, 462s. ^{1}H NMR (CDCl$_3$, δ ppm): 9.95 (s, 1H, –CHO), 7.88 (d, 1H, $J_{H–H} = 7.3$ Hz, H^3–PhCHO), 7.60 (t, 1H, $J_{H–H} = 7.3$ Hz, H^5–PhCHO), 7.52 (t, 1H, $J_{H–H} = 7.3$ Hz, H^4–PhCHO), 7.38 (m, 4H, Ph, H^{2,6}), 7.24 (m, 6H, Ph, H^{2,6}), 7.00 (d, $J_{H–H} = 7.3$ Hz, H^6-PhCHO).

2.4. Synthesis of complexes **4–6**

To a stirred solution of 0.25 mmol of copper(I) halide (24.75 mg for CuCl, 35.85.7 mg for CuBr) was suspended in 60 cm^3 of dry acetonitrile, solid 2-(diphenylphosphano)benzaldehyde (145 mg, 0.5 mmol) was suspended and the mixture was stirred for 2 h at 50 °C. The resulting clear solution was then treated with the appropriate thione (0.5 mmol) dissolved in a small amount (~20 cm^3) of methanol. The new reaction mixture was stirred for additional two hours at 50 °C and then was filtered off and left several days at ambient to provide a yellow microcrystalline product.

2.4.1. [CuBr(PCHO)(py2SH)]$_2$ (**4**)

Yellow crystals (32 mg, 23%), m.p. 179 °C; *Anal.* Calc. for $C_{48}H_{40}Br_2Cu_2N_2O_2P_2S_2$: C, 52.90; H, 3.70, N: 2.57. Found: C, 64.47; H, 4.81; N, 3.47%. IR (cm^{-1}): 3049m, 2965m, 2901m, 1691vs, 1606s, 1575vs, 1505s, 1436vs, 1366s, 1261s, 1200s, 1125vs, 1094s, 1080s, 996s, 822m, 747vs, 695vs, 521vs, 483s, 443m. ^{1}H NMR (CDCl$_3$, δ

Table 1
Crystal data and structure refinements for [CuCl(PCHO)$_2$] (**1**), [CuBr(PCHO)$_2$] (**2**) and [CuCl(PCHO)(pymtH)]$_2$ (**5**)

	1	**2**	**5**
Molecular formula	$C_{38}H_{30}ClCuO_2P_2$	$C_{38}H_{30}BrCuO_2P_2$	$C_{46.13}H_{38}Cl_2Cu_2N_4O_{2.13}P_2S_2$[a]
Formula weight	679.55	724.02	1006.63
Temperature (K)	120(2)	120(2)	120(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$	$P2_1/n$
a (Å)	11.55790(10)	18.1960(6)	14.6594(3)
b (Å)	17.1727(3)	9.8615(3)	12.0067(3)
c (Å)	16.3545(3)	19.6831(8)	24.9499(6)
α (°)	90	90	90
β (°)	101.5490(10)	116.936(1)	91.9370(10)
γ (°)	90	90	90
Volume (Å^3)	3184.03(9)	3148.76(16)	4388.95(18)
Z	4	4	4
D_{calc} (Mg/m^3)	1.418	1.527	1.523
Absorption coefficient (mm^{-1})	0.904	2.099	1.303
$F(000)$	1400	1472	2056
Crystal size (mm)	0.40 × 0.25 × 0.18	0.52 × 0.24 × 0.20	0.46 × 0.36 × 0.30
θ Range for data collection (°)	3.09–27.49	2.42–27.61	3.18–27.49
Index ranges	$-14 \leqslant h \leqslant 14$, $-22 \leqslant k \leqslant 22$, $-21 \leqslant l \leqslant 21$	$-23 \leqslant h \leqslant 23$, $-12 \leqslant k \leqslant 12$, $-25 \leqslant l \leqslant 25$	$-19 \leqslant h \leqslant 19$, $-15 \leqslant k \leqslant 15$, $-32 \leqslant l \leqslant 24$
Reflections collected	36828	28527	47805
Independent reflections	7247 [$R_{int} = 0.0439$]	3639 [$R_{int} = 0.0488$]	10023 [$R_{int} = 0.0544$]
Completeness to θ	27.49°, 99.4%	27.61°, 99.5%	27.49°, 99.4%
Data/restraints/parameters	7247/0/397	3639/0/200	10023/0/550
Maximum and minimum transmission	0.8541 and 0.6368	0.6789 and 0.5233	0.6958 and 0.5495
Refinement method	full-matrix least square on F^2	full-matrix least square on F^2	full-matrix least square on F^2
Goodness-of-fit on F^2	1.031	1.044	1.018
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0330$, $wR_2 = 0.0779$	$R_1 = 0.0261$, $wR_2 = 0.0638$	$R_1 = 0.0344$, $wR_2 = 0.0768$
R indices (all data)	$R_1 = 0.0526$, $wR_2 = 0.0845$	$R_1 = 0.0352$, $wR_2 = 0.0677$	$R_1 = 0.0529$, $wR_2 = 0.0829$
Final weighting scheme	calc $w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.7341P]$ where $P = (F_o^2 + 2F_c^2)/3$	calc $w = 1/[\sigma^2(F_o^2) + (0.0358P)^2 + 2.9145P]$ where $P = (F_o^2 + 2F_c^2)/3$	calc $w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 2.8449P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest difference in peak and hole (e Å^{-3})	0.406 and −0.522	0.305 and −0.520	0.454 and −0.419

[a] Decimal points for the number of C and O atoms due to a small impurity of doubly CHO-substituted phosphane.

ppm): 14.08 (br, 1H, NH), 10.35 (s, 1H, –CHO), 7.88 (d, 1H, $J_{H–H} = 7.3$ Hz, H^3–PhCHO), 7.60 (t, 1H, $J_{H–H} = 7.3$ Hz, H^5–PhCHO), 7.52 (t, 1H, $J_{H–H} = 7.3$ Hz, H^4–PhCHO), 7.36–7.28 (m, 10H, PPh), 7.00 (d, $J_{H–H} = 7.3$ Hz, H^6-PhCHO), 7.00 (t, 1H, H^3_{py2SH}), 6.89 (t, 1H, H^5_{py2SH}).

2.4.2. [CuCl(PCHO)(pymtH)]$_2$ (5)

Yellow crystals (25 mg, 20%), m.p. 196 °C; *Anal.* Calc. for $C_{46}H_{38}Cl_2Cu_2N_4O_2P_2S_2$: C, 55.09; H, 3.81, N: 5.59. Found: C, 54.98; H, 3.91; N, 5.66%. IR (cm^{-1}): 3054m, 2827m, 2632m, 1690vs, 1600s, 1572vs, 1479s, 1425s, 1326vs, 1196s, 1167vs, 1043s, 984s, 762s, 747s, 696vs, 528vs, 501s, 481s, 457s.

2.4.3. [CuBr(PCHO)(pymtH)]$_2$ (6)

Yellow crystals (29 mg, 21%), m.p. 191 °C; *Anal.* Calc. for $C_{46}H_{38}Br_2Cu_2N_4O_2P_2S_2$: C, 50.60; H, 3.51, N: 5.13. Found: C, 50.60; H, 3.48; N, 5.13%. IR (cm^{-1}): 3063m, 2925w, 2853w, 1677vs, 1603vs, 1584vs, 1568vs, 1474s, 1425s, 1321vs, 1210s, 1173vs, 989s, 973s, 751s, 743s, 698s, 530s, 504s, 462s.

3. Results and discussion

3.1. Synthesis

Treatment of 2-(diphenylphosphano)benzaldehyde and CuX (X = Cl, Br, I) resulted in the formation of orange-yellow colored crystalline compounds formulated as [CuX(PCHO)$_2$] (compounds **1**–**3**), regardless of the molar ratio (1:1 or 2:1) applied. Aiming to obtain phosphane/thione mixed-ligand complexes, we further treated the solutions of these precursors, skipping their isolation, with a methanolic solution of 1 equiv. of a heterocyclic thione. Stirring of such a mixture at 50 °C gradually caused slight darkening of the solution, from which, on slow evaporation, microcrystalline or powdery solids were deposited. These proved, however, to correspond to the desired pure compounds only in a few cases, although the described one-top two-step synthetic procedure applied has already produced a number of such copper(I) halide derivatives, virtually for any thione and copper(I) halide applied. In particular, pyridine-2-thione (py2SH) and pyrimidine-2-thione (pymtH) yielded small amounts of well-formed bright orange crystals, which could be satisfactory defined as compounds **4–6**, but inseparable mixtures of two or more products resulted in all the other cases. All prepared compounds are air stable diamagnetic solids, moderately soluble in acetonitrile, chloroform and acetone. Their solutions in common organic solvents are non-conducting.

3.2. Spectroscopy

The room temperature ^{1}H NMR spectra of the complexes under investigation, recorded in deuterated chloroform, are dominated by the presence of two separated multiplets in the regions $\delta = 7.40$ and $\delta = 7.25$ ppm attributed to the resonances of the non-substituted phenyl rings of the PCHO ligand. With respect to the complex multiplet assigned to the PPh_2 resonances of the un-coordinated phosphane, this splitting indicates coordination to the metal through the P atom which causes a typical upfield shift of the *ortho*-positioned protons by ca. 0.20 ppm. The resonances attributed to the formylated phenyl ring appear as well separated signals assignable to the discrete aromatic protons only for the thione-free compounds **1–3**, whereas for compounds **4–6** the extent of overlapping makes assignments of the splitting pattern for the individual phosphane and thione resonances very difficult.

The infrared spectra of compounds **1–6**, recorded in the range 4000–250 cm^{-1} display strong vibrational phosphane bands, which remain practically unshifted upon coordination. In addition, the spectra of the mixed-ligand complexes **4–6** contain the expected characteristic "thioamide bands", with shifts due to coordination indicative of an exclusive S-coordination mode. As expected, upon coordination no significant shift is noticed for the ν(C=O) vibration of the PCHO ligand.

3.3. X-ray structural investigations

The X-ray crystal structures of $[CuCl(PCHO)_2]$ (**1**), $[CuBr(PCHO)_2]$ (**2**) and $[CuCl(PCHO)(pymtH)]_2$ (**5**) (details of crystal and structure refinement are shown in Table 1) corroborate the spectroscopic results discussed above. Tables 2 and 3 list selected distances and angles of these complexes.

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

Compound **1**		Compound **2**	
Cu(1)–P(1)	2.2266(5)	Cu(1)–P(1)	2.2366(4)
Cu(1)–Cl(1)	2.2448(5)	Cu(1)–Br(1)	2.3364(4)
Cu(1)–P(2)	2.2486(5)	Cu(1)–P(1)[a]	2.2366(4)
P(1)–Cu(1)–P(2)	130.17(2)	P(1)–Cu(1)–P(1)[a]	123.53(2)
Cl(1)–Cu(1)–P(2)	108.350(18)	Br(1)–Cu(1)–P(1)	118.234(12)
P(1)–Cu(1)–Cl(1)	120.177(19)	P(1)^{1}–Cu(1)–Br(1)	118.234(12)

[a] Symmetry transformations used to generate equivalent atoms: $-x + 1$, y, $-z + 1/2$.

Table 3
Selected bond lengths (Å) and angles (°) for **5**

Cu(1)–Cl(1)	2.3350(6)	Cu(2)–S(1)	2.3608(6)
Cu(1)–P(1)	2.2506(6)	Cu(2)–S(2)	2.4227(6)
Cu(1)–S(2)	2.3469(6)	S(1)–C(20)	1.722(2)
Cu(1)–S(1)	2.4025(6)	S(2)–C(43)	1.723(2)
Cu(2)–P(2)	2.2387(6)	Cu(1)···Cu(2)	2.9766(4)
Cu(2)–Cl(2)	2.3279(6)		
S(2)–Cu(1)–S(1)	103.23(2)	P(2)–Cu(2)–S(2)	113.46(2)
P(1)–Cu(1)–S(2)	112.33(2)	Cl(2)–Cu(2)–S(2)	99.89(2)
P(1)–Cu(1)–S(1)	123.13(2)	S(1)–Cu(2)–S(2)	102.23(2)
P(1)–Cu(1)–Cl(1)	105.12(2)	C(20)–S(1)–Cu(2)	113.18(7)
Cl(1)–Cu(1)–S(1)	100.19(2)	C(20)–S(1)–Cu(1)	99.62(7)
S(2)–Cu(1)–Cl(1)	112.32(2)	C(43)–S(2)–Cu(1)	110.94(7)
P(2)–Cu(2)–Cl(2)	118.93(2)	C(43)–S(2)–Cu(2)	110.08(7)
P(2)–Cu(2)–S(1)	111.39(2)	Cu(1)–S(2)–Cu(2)	77.211(18)
Cl(2)–Cu(1)–S(1)	109.20(2)	Cu(2)–S(1)–Cu(1)	77.344(18)
Hydrogen bridges			
N(2)–H(2)	0.8800	Cl(2)···N(2)	3.0650(18)
NH(2)–Cl(2)	2.2000	Cl(2)···H(2)–N(2)	168.8
N(4)–H(4)	0.8800	Cl(12)···N(4)	3.0419(18)
NH(4)–Cl(1)	2.1600	Cl(1)···H(4)–N(4)	179.5

Compounds **1** and **2** crystallize in the monoclinic space group $P2_1/n$ and $C2/c$ respectively, both with four discrete formula units in the unit cell. Likewise, compound **5** crystallizes in the monoclinic space group $P2_1/n$ with four discrete formula units in the unit cell. It should be mentioned that there is a small impurity in the structure of **5**, indicated by the presence of a formyl substituent attached to C(25), apparently due to a small amount of doubly formylated phosphane. Hence a population parameter of 0.13 corresponds to C(47), O(3) and H(47), whereas the population parameter of H(25) is 0.87 (see also Table 1).

By comparison to the vast number of known four-coordinate species, examples of three coordination among Cu^{I} complexes are far less common, mostly represented by cations of the type CuL_3^{+}. The more rarely reported neutral complexes of the formula CuL_2X are usually formed by bulky ligands such as triarylphosphanes or aromatic amines. A literature search of published data on Cu^{I} complexes of 2-(diphenylphosphano)benzaldehyde revealed that there were structures of six cationic species known [15,16], featuring tetrahedral or trigonal planar environment around Cu^{I}, thus the three structures presented here are the first examples of neutral Cu^{I} complexes bearing PCHO.

The crystal structures of compounds **1** and **2** (Figs. 1 and 2) are quite similar having in common trigonal coordination of the copper(I) centre. Nevertheless, considering the interligand bond angles involving the central metal atom in the two structures described here, there are some

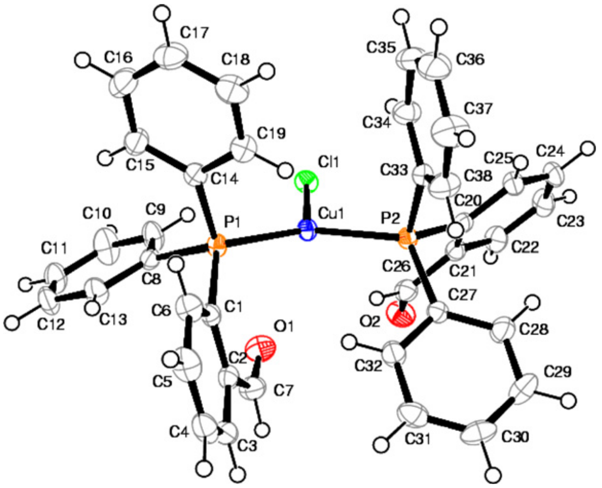


Fig. 1. A view of compound **1** with atom labels. Displacement ellipsoids are shown in the 50% probability level.

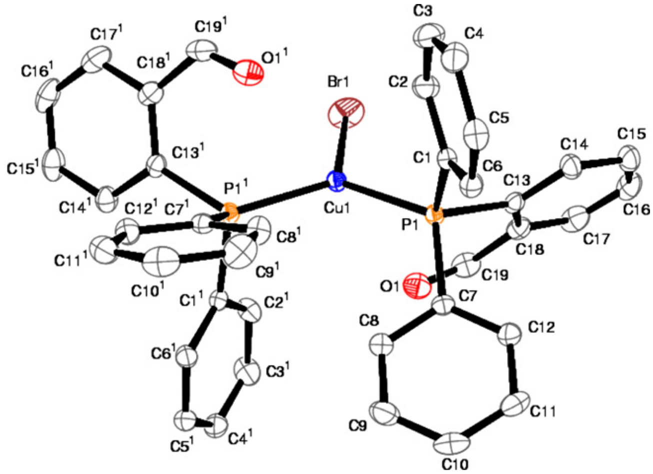


Fig. 2. A view of compound **2** with atom labels. Displacement ellipsoids are shown in the 50% probability level.

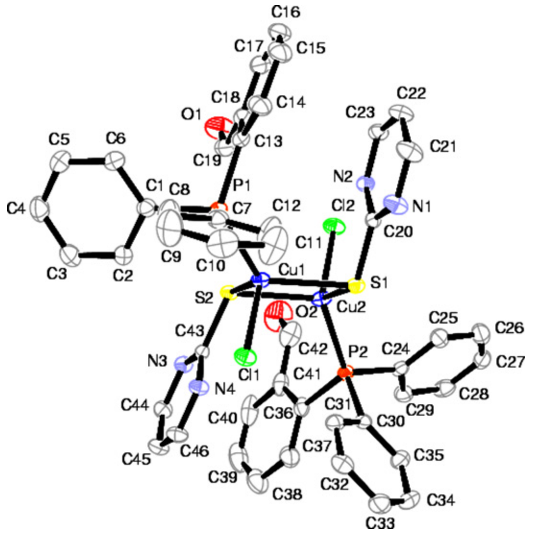


Fig. 3. A view of compound **5** with atom labels. Displacement ellipsoids are shown in the 50% probability level.

obvious differences. Thus, angular deviations from the ideal trigonal value in **1** are remarkable but not at all unexpected, at least regarding the appropriate opening up of the angle between the sterically demanding groups of the PHCO units. The sum of the three angles around Cu is 358.72°, and the Cu atom is displaced from the basal trigonal plane by 0.1465(3) Å. Another remarkable feature of **1** is the different orientation of the formyl groups of the two PCHO ligands, one of them having oriented its oxygen atom toward the copper atom to a distance of 2.804(2) Å, whereas the second one is twisted outwards. This short Cu(1)···O(1) contact is less than the sum of the van der Waal radii (1.40 (Cu) + 1.52 (O) = 2.92Å) and may be considered as a dipole–ion interaction [16,17]. The carbon–oxygen bond distance of the formyl group in the two individual PCHO units remains essential the same. Moreover, the formyl groups are both essentially coplanar with the C atoms of the attached phenyl rings.

Contrary to that, **2** exhibits a symmetric arrangement of the two PCHO units. Here the trigonal environment within the exactly planar CuP_2Br core can be considered as essentially regular with the largest P–Cu–P angle deviating only by 3.5° from the ideal trigonal expectation of 120°. The Cu–P bond distances of 2.2266(5) and 2.2448(5) Å in **1** and 2.2366(4) Å in **2** are comparable to those found in PCHO ligated cationic Cu^I complexes such as $[Cu(PCHO)_2(CH_3CN)]BF_4$ or $[Cu(PCHO)_3]BF_4$ [15]. Moreover the PCHO units have both their formyl groups oriented toward the copper atom with a short Cu···O separation of 3.002(2) Å. As a further difference between the two structures, the co-planarity within the formyl groups and the C atoms of the attached phenyl rings in **2** is substantially distorted.

In the dimeric complex **5** each copper atom displays a distorted tetrahedral environment formed by one P atom from PCHO, one Br atom and two inequivalent bridging S atoms from the thione ligands. Within the essentially planar Cu_2S_2 central core respective bond lengths and angles around the two copper atoms differ slightly. This is in contrast to other related structures with simple monodentate arylphosphane ligands like triphenylphosphane or tri-tolylphosphanes, where doubly bridging S atoms were found to generate a Cu_2S_2 rhombus with the dimeric molecule generally having a crystallographic centre of symmetry. Nonetheless, this is another example of dicopper(I) halide complex comprising a neutral thione ligand coordinated in a μ_2-S bridging mode, which is in line with our assumption that primary control of the coordination behavior (terminal or bridging) of the thione and halide ligands can be achieved by the choice of the halide ligand, with the "soft" iodide being capable to serve as bridging ligand rather than the "hard" chloride which prefers, at least in the presence of a "soft" thione-S donor atom, the terminal coordination mode [18] (Fig. 3).

An interesting structural feature within molecule **5** is the almost parallel orientation of each of the six-membered pyrimidine rings relative to the formylated phenyl ring of the respective PCHO unit. The dihedral angle between the

C13–C18 and N1,N2,C20–C23 rings is 12.68(8)° and the dihedral angle between rings C36–C41 and N3,N4,C43–C46 is 16.12(5)°. The respective stacking distances between ring centroids are 3.743(1) and 3.728(1) Å, respectively, suggesting the presence of significant $\pi \cdots \pi$ interactions [19]. These may be considered to significantly contribute, together with the intramolecular hydrogen bonds (see Table 3), to the alignment of the molecule in the crystalline state.

4. Conclusion

The aim of this work was the study of the coordination capability of 2-(diphenylphosphano)benzaldehyde (PCHO) toward copper(I) halides. We have found that PCHO acts as a monodentate, coordinating to the metal exclusively via the "soft" phosphorus atom, whereas no bonding interaction could be proposed for the formyl group, despite the observed marked orientation of its oxygen atom towards the copper centre. Thus, the resulting complexes of composition $[CuX(PCHO)_2]$, are monomers with the copper atom in a fairly trigonal environment. These compounds prove to be good precursors for the preparation of other derivatives; in the course of the present study these are chosen for the synthesis of mixed-ligand dimeric complexes, which contain, besides the PCHO unit, a heterocyclic thioamide. The structure of the mixed-ligand complex presented here, comprising the neutral thione ligand coordinated in a μ_2-S bridging mode, confirms once more our assumption that primary control of the coordination behavior (terminal or bridging) of the thione and halide ligands in such dimers can be achieved by the choice of the halide.

Acknowledgement

We thank the EPSRC X-ray crystallography service at the University of Southampton for collecting the X-ray data.

Appendix A. Supplementary material

CCDC 612610, 612611 and 612609 contain the supplementary crystallographic data for **1**, **2** and **5**. 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.2007.09.001.

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