New copper(I) chloride complexes with heterocyclic thiones and triphenylphosphine as ligands. Crystal structures of $[Cu(PPh_3)_2(bzimtH_2)Cl]\cdot CH_3COCH_3$ and $[Cu(PPh_3)_2(nbzimtH_2)Cl]$

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Abstract

Copper(I) chloride complexes with various heterocyclic thiones and triphenylphosphine as ligands were prepared and characterized by elemental analysis, IR, UV–Vis and NMR spectroscopies. Crystal structures of the title compounds (complexes **A** and **B**, respectively) were determined by X-ray analysis. Crystals of complex **A** are yellow, monoclinic, space group $P2_1/c$ with $a = 13.147(2)$, $b = 18.592(3)$, $c = 17.259(3)$ Å, $\beta = 97.45(2)°$, $Z = 4$. The final R value is 0.036 ($R_w = 0.036$, $gof = 1.8$). Crystals of complex **B** are yellow, triclinic, space group $P\bar{1}$ with $a = 10.815(6)$, $b = 13.109(2)$, $c = 18.211(3)$ Å, $\alpha = 110.87(1)$, $\beta = 100.55(4)$, $\gamma = 91.97(4)°$, $Z = 2$. The final R value is 0.060 ($R_w = 0.062$, $gof = 1.7$). In both cases the asymmetric units include one complex molecule in which the $bzimtH_2$ or $nbzimtH_2$ act as monodentate ligands through the sulfur atom, as well as one solvent molecule (CH_3COCH_3) in the case of complex **A**.

Introduction

In previous work [1–6] we have considered the physical and structural properties of some complexes formed by copper salts and heterocyclic thiones. Our purpose is to investigate ligand behaviour in connection with different factors such as the complexing properties of the ligands containing N, S and P as donors and the experimental conditions employed in the synthesis reactions. Continuing our investigation of this search we report results on the synthesis and structural characterization of some new complexes formulated as $[Cu(PPh_3)_2(L)Cl]$. The X-ray structure analysis of $[Cu(PPh_3)_2(bzimtH_2)Cl]$ as acetone solvate (complex **A**) and $[Cu(PPh_3)_2(nbzimtH_2)Cl]$ (complex **B**) has been undertaken in order to provide detailed information on the coordination geometry and to verify the conclusions drawn from spectroscopical studies.

Experimental

Starting materials

All thione ligands, supplied by EGA or Aldrich, were purified by recrystallization from ethanol. Anhydrous copper(I) chloride, triphenylphosphine and all solvents were of reagent grade and were used without further purification.

Preparation of the complexes

CuCl (1 mmol) was suspended in 30 ml acetone and treated with a 60 ml solution of 1 mmol of the appropriate ligand in 2 mmol PPh_3 in the same solvent. The reaction mixture was stirred for 1 h at 40 °C, filtered and allowed to evaporate slowly at room temperature. The microcrystalline solid thus formed was collected by filtration, washed with small amounts of ethanol and ether and dried in vacuum.

Crystal and molecular structure determination

Crystals were obtained by slow evaporation of an acetone solution of the two complexes. X-ray data were collected at room temperature in the $\omega - 2\theta$ scan mode ($\theta \leqslant 70$) on an Enraf-Nonius

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TABLE 1. Experimental data

	Complex **A**	Complex **B**
Formula	$CuClSP_2N_2C_{43}H_{36}$	$CuClSP_2N_3O_2C_{43}H_{35}$
Formula weight	773.8	818.8
Space group	$P2_1/c$	$P\bar{1}$
Cell dimensions		
a (Å)	13.147(2)	10.815(6)
b (Å)	18.592(3)	13.109(2)
c (Å)	17.259(3)	18.211(3)
α (°)		110.87(1)
β (°)	97.45(2)	100.55(4)
γ (°)		91.97(4)
Z	4	2
D_x (g cm^{-3})	1.320	1.153
Total reflections	6330	8227
Significant reflections ($I \geqslant 3\sigma(I)$)	4702	4526
Refined parameters	613	478
Residual factors		
R	0.036	0.060
R_w	0.036	0.062
gof	1.8	1.7

CAD4 diffractometer equipped with graphite monochromator and Cu-target X-ray tube ($\lambda = 1.5418$ Å). Intensity data were corrected for Lorentz and polarization effects. The absorption was disregarded. Cell dimensions together with other experimental parameters are indicated in Table 1.

Only reflections with $I \geqslant 3\sigma(I)$ were retained for the solution of the structures using the SDP software package [7]. *E*-maps revealed all non-hydrogen atoms, and all hydrogen atoms appeared on difference maps.

Refined parameters [8] were calculated by using anisotropic thermal parameters for non-hydrogen atoms, and isotropic factors for hydrogen atoms. The residual factors are indicated in Table 1. See also 'Supplementary material'.

Physical measurements

Elemental analyses were performed on a Perkin-Elmer 240 B elemental analyser. IR spectra were recorded in the 4000–250 cm^{-1} region on a Perkin-Elmer 467 spectrophotometer using KBr pellets. Electronic spectra, in chloroform solutions, were obtained on a Cary 17 DX spectrophotometer. NMR spectra were recorded on a Bruker AW 80 spectrophotometer. Melting points were determined with a Buchi apparatus and are uncorrected.

Results and discussion

The new tetrahedral mononuclear copper(I) complexes of the general formula $[Cu(PPh_3)_2(L)Cl]$ were prepared by a method widely used by us previously, namely, the reaction between the Cu(I) salt and a 1:2 mixture of the heterocyclic thione and triphenylphosphine. Table 2 lists the compounds with their colours, melting points and analytical data. All the complexes isolated are air stable crystalline solids ranging in colour from white to yellow; their solutions turn to green after two weeks.

Description of the structures

Main bond lengths and angles are given in Tables 3 and 4 for the complexes **A** and **B**, respectively. Figures 1 and 2 illustrate the molecular configurations of the complexes together with their respective labelling schemes. Both complexes are composed of closely packed monomeric molecules of $[Cu(PPh_3)_2(L)Cl]$ where

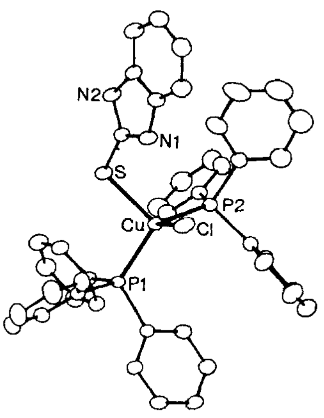

Fig. 1. ORTEP representation of $[Cu(PPh_3)_2(bzimtH_2)Cl]$.

TABLE 2. Some physical properties and analytical data of the complexes

Compound	Yield (%)	Color	Melting point (°C)	*Anal.* Found (calc.) (%)			
				C	N	H	Cu
$[Cu(PPh_3)_2(py2SH)Cl]$	85	yellow	159	66.98(66.97)	1.91(1.91)	4.76(4.76)	8.50(8.65)
$[Cu(PPh_3)_2(pymtH)Cl]$	78	orange	199	65.94(65.26)	3.86(3.80)	4.36(4.62)	9.15(8.63)
$[Cu(PPh_3)_2(tzdtH)Cl]$	56	white	197	63.80(63.00)	2.14(1.88)	5.08(4.71)	8.85(8.55)
$[Cu(PPh_3)_2(bzimtH_2)Cl]$	60	yellow	209	66.88(66.60)	1.73(1.82)	4.67(4.52)	7.53(8.20)
$[Cu(PPh_3)_2(bztzH)Cl]$	75	yellow	156	66.14(65.24)	2.30(1.77)	4.45(4.26)	7.88(8.03)
$[Cu(PPh_3)_2(bzoxtH)Cl]$	62	white	162	66.88(66.60)	1.72(1.82)	4.67(4.52)	7.83(8.20)
$[Cu(PPh_3)_2(nbzimtH_2)Cl]$	82	yellow	105	62.23(63.03)	4.86(5.13)	4.67(4.28)	7.82(7.76)
$[Cu(PPh_3)_2(quotH_2)Cl]$	80	yellow	204	64.97(65.84)	3.55(3.49)	4.36(4.49)	7.75(7.92)

TABLE 3. Selected interatomic distances (Å) and angles (°) for $[Cu(PPh_3)_2(bzimtH_2)Cl]$

Bonds			
Cu-P1	2.278(1)	N1-C37	1.347(5)
Cu-P2	2.295(1)	N1-C38	1.385(5)
Cu-S	2.377(1)	N2-C37	1.334(5)
Cu-Cl	2.376(1)	N2-C43	1.392(5)
P1-C1	1.820(3)	C38-C39	1.401(5)
P1-C7	1.836(3)	C39-C40	1.356(8)
P1-C13	1.835(3)	C40-C41	1.375(8)
P2-C19	1.827(6)	C41-C42	1.386(6)
P2-C25	1.837(4)	C42-C43	1.382(6)
P2-C31	1.834(4)	C43-C38	1.362(6)
S-C37	1.689(4)		
Angles			
Cl-Cu-S	106.62(4)	Cu-P2-C19	112.5(1)
Cl-Cu-P1	111.47(4)	Cu-P2-C25	117.7(1)
Cl-Cu-P2	103.67(4)	Cu-P2-C31	115.9(1)
S-Cu-P1	103.03(4)	Cu-S-C37	106.4(1)
S-Cu-P2	109.62(4)	S-C37-N1	126.0(3)
P1-Cu-P2	121.71(3)	S-C37-N2	127.5(3)
Cu-P1-C1	115.5(1)	C37-N1-C38	110.2(3)
Cu-P1-C7	118.1(1)	N1-C37-N2	106.5(3)
Cu-P1-C13	112.7(1)		

TABLE 4. Selected interatomic distances (Å) and angles (°) for $[Cu(PPh_3)_2(nbzimtH_2)Cl]$

Bonds			
Cu-P1	2.265(2)	N1-C38	1.368(1)
Cu-P2	2.282(2)	N2-C37	1.34(1)
Cu-S	2.381(2)	N2-C43	1.365(8)
Cu-Cl	2.384(2)	C38-C39	1.36(1)
P1-C1	1.828(8)	C39-C40	1.37(1)
P1-C7	1.816(6)	C40-C41	1.38(1)
P1-C13	1.819(7)	C41-C42	1.37(1)
P2-C19	1.827(6)	C42-C43	1.38(1)
P2-C25	1.822(8)	C43-C38	1.37(1)
P2-C31	1.829(7)	N3-C40	1.46(1)
S-C37	1.686(7)	N3-O1	1.23(1)
N1-C37	1.319(9)	N3-O2	1.20(1)
Angles			
Cl-Cu-S	108.09(7)	Cu-P2-C25	113.5(2)
Cl-Cu-P1	110.41(7)	Cu-P2-C31	114.7(2)
Cl-Cu-P2	103.75(8)	Cu-S-C37	105.0(3)
S-Cu-P1	100.86(9)	S-C37-N1	128.8(6)
S-Cu-P2	108.21(8)	S-C37-N2	124.6(6)
P1-Cu-P2	124.75(7)	C37-N1-C38	110.7(4)
Cu-P1-C1	114.5(2)	N1-C37-N2	106.6(6)
Cu-P1 C7	113.6(2)	O1-N3-O2	123.5(9)
Cu-P1-C13	116.8(3)	C40-N3-O1	118.0(1)
Cu-P2-C19	117.5(3)	C40-N3-O2	118.6(8)

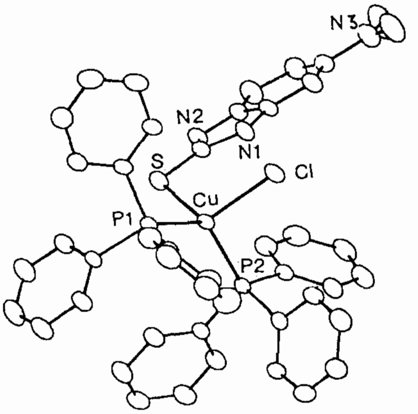

Fig. 2. ORTEP representation of $[Cu(PPh_3)_2(nbzimtH_2)Cl]$.

L = $bzimtH_2$ and $nbzimtH_2$. The structure of **A** contains an acetone molecule hydrogen bonded to the complex. Although these complexes have different structural parameters, there are only few variations in bond lengths and bond angles between them. In both cases the Cu atom is surrounded, in the form of a distorted tetrahedron, by two phosphorus atoms, one sulfur and one chlorine atom.

The observed Cu-S distances of 2.381(2) and 2.376(1) Å are consistent with the distances usually found for tetrahedrally coordinated copper(I) with thione-S donors [5, 9, 10].

The Cu-P1 and Cu-P2 distances of 2.278(1) and 2.295(1) Å in **A** and 2.265(2) and 2.282(2) Å in **B** are in good agreement with previous values obtained for Cu–P bonds [6, 9–12]. Nevertheless, the shorter Cu–P distances found in the complexes [Cu(p-$CH_3C_6H_4)_3P$(pymtH)]$_2$ (2.227(1) Å) [13] and [Cu(p-$CH_3C_6H_4)_3P$(tzdtH)]$_2$ (2.222(1) Å) [14] are probably the result of the strong π-electron acceptor properties of the phosphine ligand, resulting in a relatively stronger Cu–P bond. These differences are reflected substantially on the metal–phosphine ratio according to the conclusion of Lippard and Palenik [15]. In fact, the increased number of phosphorus atoms around the metal must result in a decrease in Cu–P backdonation and consequently in an increase in bond length, because of a reduced π-bonding contribution.

The Cu–Cl distance of 2.376(1) in **A** and 2.384(2) Å in **B** are slightly longer than those observed in the complex [Cu($PPh_3)_2$(py2SH)Cl] [9].

The range of C–N distances in the free imidazole ring (1.36–1.40 Å) [16, 17] is smaller than that observed in the coordinated ligand in complexes **A** and **B** (1.33–1.40 Å). This result indicates the less aromatic character of the complexed ligand. The slightly longer C–S distance (1.69 compared to 1.67 Å) in the complex indicates less double bond character than in the free ligand.

As in the structure of the complex [Cu($PPh_3)_2$(py2SH)Cl] [9] three of the angles in the CuP_2SCl group are nearly those of a regular tetrahedron while the P1–Cu–P2 angle deviates considerably from 109.47°. Namely, in both molecules this angle shows a distortion away from the ideal tetrahedral geometry with a value of 121.71(3)° for complex **A** and 124.75(7)° for complex **B**. These values are close to trigonally coordinated Cu(I), a mode which is essentially determined by the steric bulky ligands and the constraints related to intramolecular hydrogen bridging bonds.

In both complexes, Cl is hydrogen bonded to the imidazoline NH atom with Cl···N distances of 3.02 in **A** and 3.07 Å in **B**. These hydrogen bonds must be the main reason for the conformational changes, e.g. increase of the P–Cu–P angle and distortion from the tetrahedral configuration. This hydrogen bonding influences also the orientation of the complexed ligands.

Spectroscopical studies

The solid state IR spectra, in the region 4000–250 cm^{-1}, are in agreement with the X-ray diffraction data with respect to the mode of coordination. The spectra of all complexes show a broad peak of moderate intensity in the 3180–3140 cm^{-1} range, corresponding to the (NH) stretching and with no significant shift from the free ligand values. This indicates that the ring nitrogen does not take part in the coordination.

The predominance of the thione form of the ligands investigated, as well as their monodentate sulfur donating character is further supported by the presence of the four characteristic 'thioamide bands' and by consideration of their behaviour upon coordination [18, 19]. In fact, 'thioamide I' shows only small (± 5 cm^{-1}) shifts, signifying that the ligands are not N-bonded to the metal. On the contrary, a very strong band in the 1000 cm^{-1} region assignable to 'thioamide III', gets shifted by 20–70 cm^{-1} to the lower-frequency side in the spectra of the complexes. Since this band has been associated with the stretching vibration of the carbon–sulfur bond, the lowering of the bond order of C=S indicates the presence of an M–S contact.

In all the spectra of the complexes the presence of triphenylphosphine can easily be identified from the appearance of very strong characteristic bands in the 520–485 cm^{-1} range. Finally, the IR spectra of the thione complexes show one additional band of moderate intensity at 350 cm^{-1}, which is absent in the spectra of the ligand and, therefore, may be assigned to the ν(Cu–S) vibration [18].

The electronic spectra of the compounds in $CHCl_3$ solutions, as expected, show no d–d transitions, but a strong absorption in the 300–360 nm region in addition to an absorption at 260–280 nm, which can be assigned to intraligand transition processes.

The ^{1}H NMR spectra of the compounds in $CDCl_3$ solution also support the predominance of the thione tautomer by exhibiting a signal for the NH group at 10–14 ppm in connection with the absence of the corresponding SH proton. The broad nature of the signal implies the occurrence of hydrogen bonds. All other signals expected for the thione and PPh_3 ligands are observed.

Supplementary material

All the crystallographic material (atomic coordinates, bond lengths, bond angles and equivalent thermal factors) have been deposited with the Cambridge Crystallographic Data Centre.

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