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STRUCTURE OF TWO NEW COMPOUNDS OF COPPER(I) IODIDE WITH N-DONOR AND P-DONOR LIGANDS

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The copper(I) halides complexes present a large structural variety and have numerous technological applications. In this work we have prepared two new copper(I) complexes with N-donor and P-donor ligands [CuI(2-(diphenylphosphino)benzaldehyde)$_2$] (**1**), [CuI(2-(diphenylphosphino)benzaldehyde)(acetonitrile)]$_2$ (**2**) from CuI as starting material. The complexes were characterized by elemental analysis, IR spectroscopy and crystallographic studies. Compound **1** crystallizes in a monoclinic $C2/c$ space group. It is a monomer with a P-donor ligand bound with copper(I) in a distorted triangular planar geometry. Compound **2** crystallizes in monoclinic $P2_1/c$ space group. It has two molecules of the P-donor ligand and two molecules of the N-donor ligand in *trans* configuration, forming a dimer with two bridging iodides. The Cu(I) atom is four coordinated in trigonal pyramidal geometry with τ_4 value of 0.85. The bond distances are 2.5050(6)-2.7090(6) Å for Cu–I, 2.044(4) Å for Cu–N and 2.2489(8)-2.2528(8) Å for Cu–P.

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INTRODUCTION

The copper(I) complexes have been object of study in the last years due to the great variety of photo-physical and photo-chemical properties that they exhibit [1-10]. These complexes have potential technological applications in photovoltaic devices, biosensors, OLEDs and photochemical catalysis, among others [11-26]. From the economic point of view, Cu is more abundant and less expensive than noble metals or rare earth metals. In addition, Cu complexes show antitumor, anti-inflammatory and antimicrobial activities [27-35]. Cu is an essential microelement and is much less toxic than non-endogenous metals like platinum or ruthenium [36].

Cu(I) coordination chemistry is very interesting due to the favourable soft acid-soft base interactions with ligands containing nitrogen, phosphorus and sulphur donor atoms. When these ligands are combined with copper(I) halides, they produce a vast number of complexes with an extraordinary stoichiometric and geometrical variety. There are numerous monomeric, square dimeric, cubane tetrameric, zig-zag polymeric and "stair step" polymeric structures [37]. This versatility is strongly affected by such factors as temperature, reaction stoichiometry, solvents used in the synthesis etc [38-45].

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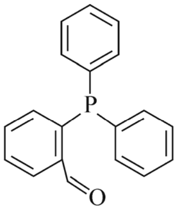
Organophosphane Cu(I) halides were extensively studied in the past [46-48], and for many potentially polydentate ligands variable metal: ligand stoichiometry has been achieved and crystal structures determined. Luminescence properties have started to be explored only recently [49, 50]. In this paper, we report the synthesis and structural characterization of two new copper(I) complexes with 2-(diphenylphosphino)benzaldehyde (Scheme 1) where the influence of the solvent used is remarkable [51].



2-(Diphenylphosphino)benzaldehyde

Scheme 1.

EXPERIMENTAL

Materials and methods. All syntheses were carried out at room temperature under aerobic conditions in commercial-grade solvents. Reagents were used as purchased (ALDRICH) without further purification. Elemental analyses were performed on an Elemental CNHS FLASH EA 1112 Elemental analyser. IR spectra were recorded on a Nicolet IR spectrophotometer. X-ray analysis was performed with a Rigaku Oxford Diffraction Supernova diffractometer.

[CuI(2-(diphenylphosphino)benzaldehyde)$_2$] (1). A solution of CuI (0.2 g, 1.05 mmol) in toluene (50 ml) was mixed with 2-(diphenylphosphino) benzaldehyde (0.15 g, 0.52 mmol) also dissolved in toluene (20 ml). The solution is stirred for 1 hour at room temperature. After this time, a yellow precipitate is produced which is collected and dissolved in dichloromethane. After three days, single crystals suitable for X-ray diffraction were obtained by slow evaporation of the dichloromethane. Yield (82%). Elemental analysis calc. for $C_{38}H_{30}CuIO_2P_2$ (**1**) ($M = 771.00$) (%): C 59.17, H 3.92. Found (%): C 58.62, H 3.66. IR (KBr, cm^{-1}): 2368.96, 2341.37, 1736.58, 1721.09, 1703.87, 1690.10, 1655.66, 1560.97, 1545.48, 1459.39, 1438.73, 1288.95, 1121.95, 1075.46, 1023.81.

[CuI(2-(diphenylphosphino)benzaldehyde)(acetonitrile)]$_2$ (2). A solution of CuI (0.2 g, 1.05 mmol) in acetonitrile (50 ml) was slowly added to a solution of 2-(diphenylphophino)benzaldehide (0.15 g, 0.52 mmol) in acetonitrile (20 ml). The solution is stirred for 1 hour at room temperature. After a few days, single crystals suitable for X-ray diffraction were grown by slow evaporation of the solvent. Yield (95%). Elemental analysis calc. for $C_{21}H_{18}CuINOP$ (**2**) ($M = 521.77$) (%): C 48.32, N 2.68, H 3.48. Found (%): C 49.05, N 2.93, H 3.07. IR (KBr, cm^{-1}): 2827.13, 2746.14, 1685.48, 1643.05, 1581.34, 1477.20, 1430.92, 1396.21, 1288.22, 1257.36, 1199.51, 114.65, 1091.51, 1025.94, 995.09.

X-ray crystallography. X-ray diffraction (XRD) measurements was made at room temperature using a Rigaku Oxford Diffraction SuperNova diffractometer equipped with an ATLAS detector (CCD) and Cu radiation micro-source ($\lambda = 1.5418$ Å) at X-ray Service from La Laguna University (SIDIX). CrysAlisPro [52] software was used to process the data. The structures were determined by a dual-space algorithm using the SHELXT program [53], and refinement was performed using SHELXL program [54] against F^2 by full-matrix least-squares refinement. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in the model at calculated positions, and refined with a rigid model with their U_{iso} value to $1.2U_{\text{eq}}$ of their parent atoms. The PLATON program [55] has been used for geometric calculations while OLEX2 [56] program was used for graphics. Crystal data, data collection and structure refinement details are summarized in Table 1.

Crystallographic data for structures reported in this paper have been deposited in the Cambridge Crystallographic Data Centre with reference numbers 1811558 and 1811557 respectively. Copies of the data can be obtained free of charge on application to the CCDC, Cambridge, U.K. (http://www.ccdc.cam.ac.uk/).

TABLE 1. Summary of the Crystal Data for **1**, **2** Compounds

Parameter	**1**	**2**
CCDC	1811558	1811557
Empirical formula	$C_{38}H_{30}CuIO_2P_2$	$C_{21}H_{18}CuINOP$
Formula weight	771.00	521.77
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
a, b, c, Å; β, deg.	18.2829(7), 10.1687(2), 19.6998 (7); 115.961(5)	9.4269(2), 16.8128(3), 13.2655(3); 106.857(2)
V, Å^3	3292.9(2)	1072.22(13)
Z	4	4
D_{calc}, g/cm^3	1.555	1.722
$\mu(\text{Cu}K_\alpha)$, mm^{-1}	9.47	14.40
$F(000)$	1544	1024
Crystal dimensions, mm	0.15×0.09×0.07	0.12×0.09×0.06
Theta range for data collection, deg.	5.0-73.2	3.5-73.5
Limiting indices	$-22 \le h \le 20$, $-8 \le k \le 12$, $-20 \le l \le 24$	$-11 \le h \le 8$, $-19 \le k \le 20$, $-15 \le l \le 16$
Reflections (collected / unique, R_{int})	5794 / 3189 (0.017)	7889 / 3952 (0.025)
Data / restraints / parameters	3189 / 0 / 200	3952 / 0 / 236
R_1[a], wR_2[b] ($F^2 > 2\sigma(F^2)$)	0.032, 0.092	0.026, 0.065
Goodness-of-fit on F^2	1.02	1.03
Largest diff. peak and hole, e/Å^3	0.98 and –0.58	0.55 and –0.43

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[a] $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_c|$.

[b] $wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma w(F_0^2)^2\}^{1/2}$.

RESULTS AND DISCUSSION

Preparation of the complexes. The synthetic procedure for the preparation is straightforward and involves mixing together an equimolar amount of CuI with the P-donor ligand in acetonitrile or dichloromethane and stirring the slurry for 1 hour at room temperature. After a few days suitable single crystals for X-Ray Crystallography were obtained by slow evaporation of the solvent. The iodide ligand stabilises well the oxidation state Cu(I) and no oxidation was observed during the synthetic procedure. However, in related syntheses when chloride or bromide are used as halides a colour change to green [57] indicating oxidation of Cu(I) to Cu(II) was observed. In the preparation of Cu(I) halide complexes the structure is highly affected by the solvent and by metal: ligand the ratio.

Crystal structure. The crystallographic data and structure refinement parameters are summarized in Table 1, and selected bonds and angles for all compounds are listed in Table 2.

Compound **1** (Fig. 1) is a three-coordinated metal complex. The central atom of Cu(I) is surrounded by three atoms, two P-donors and one iodide. The Cu(I) environment shows a distorted triangular planar coordination. The ideal value for a perfect trigonal planar geometry is 120°, and the bond angle for P–Cu–P^i is 124.16(5)°. This angular distortion is due to 2-(difenylphosphine)benzaldehyde being a bulky ligand, and in this way the steric repulsion is minimized. The phosphorus atoms have a tetrahedral coordination, to copper atom plus three carbon atoms. This coordination environment can be described by a single geometric index called τ_4 [58] that takes the value of 1.0 for perfect tetrahedral configuration, while it is 0.0 in the case of perfect square. For intermediate configurations such as trigonal pyramidal, the τ_4 parameter will have a value between 0.0 and 1.0. In **1** the τ_4 value is 0.86 indicating a distorted trigonal pyramidal configuration. The formyl

TABLE 2. Selected Bond and Angles for **1**, **2**

Distances, Å		Angles, deg.			
		Complex **1**			
I1–Cu1	2.5050(6)	$P1^{i}$–Cu1–I1	117.92(2)		
Cu1–P1	2.2489(7)	P1–Cu1–I1	117.92(2)		
Cu1–$P1^{i}$	2.2489(7)	P1–Cu1–$P1^{i}$	124.16(5)		
		Complex **2**			
I1–Cu1	2.6437(5)	Cu1–I1–$Cu1^{ii}$	75.326(16)	I1–Cu1–$I1^{ii}$	104.674(16)
Cu1–$I1^{ii}$	2.7093(5)	N1–Cu1–I1	103.52(9)	N1–Cu1–$I1^{ii}$	106.08(9)
Cu1–P1	2.2530(7)	P1–Cu1–I1	119.92(2)	P1–Cu1–$I1^{ii}$	108.96(2)
Cu1–N1	2.046(3)	N1–Cu1–P1	112.62(9)		

Symmetry code: ^{i} $-x+1, y, -z+3/2$; ^{ii} $-x+2, -y+1, -z+1$.

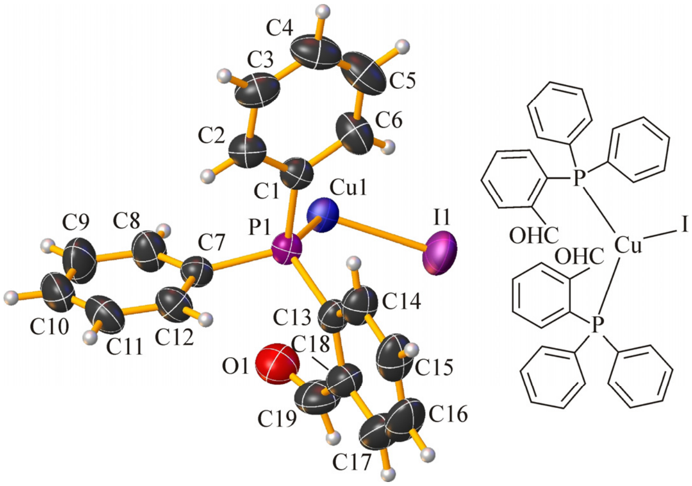

Fig. 1. View of the asymmetric unit of compound **1**. Atom labelling is shown.

groups of the two 2-(diphenylphosphino)benzaldehyde ligands have both their oxygen atom oriented toward the copper atom, similar to the other structures [59]. The Cu…O distance is 3.057 Å, shorter than the sum of the respective Van der Waal radii (3.24 Å), and can be considered as a ion-dipole interaction. Moreover, the formyl groups are coplanar with the C atoms of the attached phenyl ring. The geometric parameters agree with the values reported for CuI adducts with similar organic ligands in the CSD Database (Version 5.39) [60, 61]. The bonds distances obtained for Cu–I and Cu–P are 2.5050(6) Å and 2.2489(7) Å, respectively. These values are close to average values extracted from CSD Database, 2.54(3) Å for Cu–I and 2.25(2) Å for Cu–P. The P–Cu–I and P–Cu–P angles are 117.92(2)° and 124.16 (5)°, the average values calculated from CSD are 115(4)° and 128(8)°, respectively.

Compound **2** (Fig. 2) exhibits a square dimer configuration formed by Cu–P (2-(difenyphosphine)benzaldehyde), Cu–N(acetonitrile) and Cu–I bonds. The phosphorus and nitrogen atoms adopt *trans* configuration similar to other related structures [62]. The copper and iodine atoms form a four membered coplanar ring. Copper atoms have fourfold coordination and can be described by τ_4 geometric index. In this complex the τ_4 value is 0.85, indicating a perfect trigonal pyramidal configuration. As in **1**, the phosphorus atoms are tetracoordinated with τ_4 value of 0.84, indicating a distorted trigonal pyramidal configuration. The geometric parameters for **2** are similar to the values reported in CSD Database [63, 64]. For Cu–I distances, we found 2.6437(5) Å, for Cu–P distances - 2.253(7) Å, and 2.046(3) Å for Cu–N, in good agreement with the averaged values from CSD, 2.70(7) Å, 2.25(3) Å and 2.03(2) Å, respectively. For angles, the value for I–Cu–I is

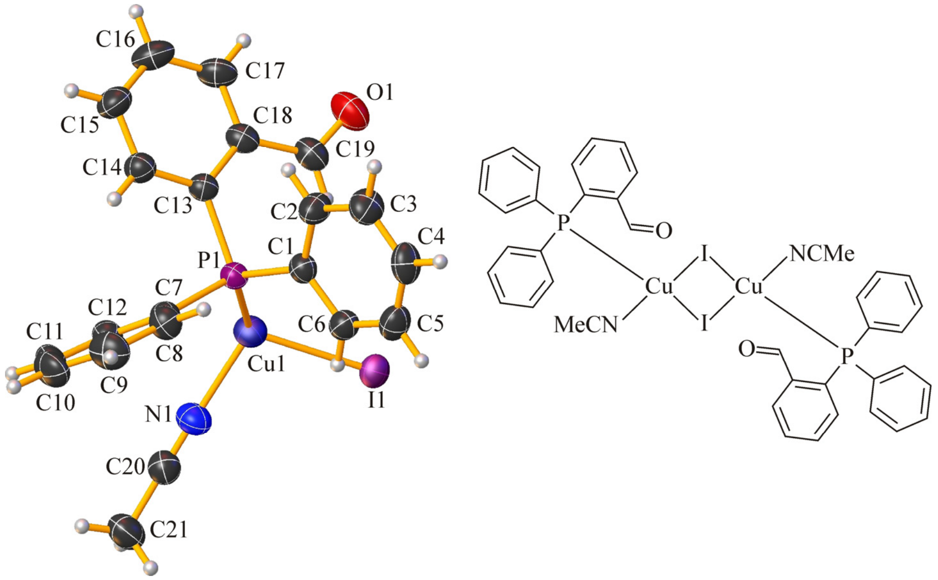

Fig. 2. View of the asymmetric unit of compound **2**. Atom labelling is shown.

104.674(16)°, matching the average value reported in CSD, 106(6)°. The Cu···Cu distance is 3.2712(7) Å and I···I distance is 4.2376(4) Å, while the corresponding averages in CSD are 3.0(3) Å and 4.29(13 Å.

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