ЖУРНАЛ СТРУКТУРНОЙ ХИМИИ

2014. Том 55 *Приложение № 2* *S303 – S307*

UDC 548.73:547.13:546.56

SYNTHESIS AND STRUCTURE OF [CuI(3-METHYL-2-PHENYLPYRIDINE)$_2$] WITH INTERMOLECULAR STACKING INTERACTIONS

R. Hernández Molina[1,2], A. Agirretxu[3], J. González-Platas[4]

[1]*Departamento de Química Inorgánica, Facultad de Farmacia, Universidad de La Laguna, Tenerife, Spain*
E-mail: rrhernan@ull.es
[2]*Instituto Universitario de Química Bioorgánica Antonio González, La Laguna, Tenerife, Spain*
[3]*Departamento de Física, Universidad de La Laguna, Tenerife, Spain*
[4]*Departamento de Física, Servicio de difracción de Rayos X (SIDIX), Universidad de La Laguna, Tenerife, Spain*

Received April, 23, 2014

The preparation of a copper(I) iodide complex with a N-donor ligand 3-methyl-2-phenylpyridine of formula [CuI(3-methyl-2-phenylpyridine)$_2$] is described. The isolated complex was characterized by elemental analyses, IR spectroscopy and crystallographic studies. Single crystal X-Ray diffraction analysis of the complex reveal their monomeric tri-coordinated nature. The coordination polyhedron around the copper center may be described as a distorted trigonal planar geometry. The Cu—N distances for this compound are 1.984(7) and 1.982(7) Å, while the Cu—I distance is 2.5507(9) Å.

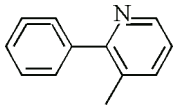
K e y w o r d s: copper(I), halides, structure, mononuclear complexes.

INTRODUCTION

Copper(I) halides aggregates constitute an interesting family of compounds due to their photophysical and photochemical properties [1—10]. This class of compounds is attracting renewed interest [11—15] because of its potential applications in high efficiency OLEDs [16—18]. Coordination systems based on copper halides show a remarkable structural diversity [14] which arises from the many possible combinations of coordination numbers (two, three and four) available for copper(I) and for the geometries that can be adopted by the halide ions (from terminal to μ_2- and up to μ_8-bridging modes). Its coordinative lability allows copper(I) to play a significant role in many catalytic and stoichiometric processes, including catalytic hydrocarbon functionalization reactions [19], catalytic oxidation reactions [20] and biomimetic dioxygen activation [21].

Organophosphine copper(I) halides have been extensively studied in the past [22—24] and several species with different metal coordination numbers and metal:ligand stoichiometries have been already synthesized and the crystal structures determined. The luminiscence properties has only been explored recently [25, 26] and can play a role in the photophysics of the complexes.

We have been interested in the preparation of copper(I) with N-donor ligands to explore the luminescence properties exhibited by these complexes [27—29]. The structures of these compounds are influenced by factors such as the ligands and solvents used, temperature, ratio metal:ligand, thus giving a variety of coordination geometries. Halide copper(II) complexes have also been extensively studied [30—37] especially those containing chloro and bromo ligands. In this paper we report the synthesis, structural characterisation of a mononuclear copper(I) complex derived from CuI and 3-methyl-2-phenylpyridine.



EXPERIMENTAL

Preparation of [CuI(3-methyl-2-phenylpyridine)$_2$]. CuI (0.2 g, 1.39 mmol) dissolved in acetonitrile (60 ml) was mixed with 3-methyl-2-phenylpyridine (scheme 1) (0,23 g, 1.39 mmol) dissolved in acetonitrile (20 ml). The mixture was stirred at room temperature for 3 h. After a few days single crystals suitable for X-Ray diffraction were grown by slow evaporation of the solvent. Anal. calc. for $CuC_{24}N_2H_{22}I$ C, 54.5; H, 4.19; N, 5.29 %. Found: C: 54, 29; H, 3,84; N, 5.96 %. IR (KBr, cm^{-1}): 3419, 2920, 2361, 1631, 1453, 1380, 1120.

MATERIALS AND METHODS

All syntheses were carried out at room temperature using commercial-grade solvents and reagents used as purchased (ALDRICH) without further purifications. Elemental analyses were performed on Elemental CNHS FLASH EA 1112 Elemental analyzer. IR spectra were recorded on a Nicolet IR spectrophotomer.

Single crystal X-ray crystallography. The XRD data for this compound was collected at 295(2) K with an Agilent SuperNova diffractometer with micro-focus X-ray using Mo radiation (λ = 0.71073 Å) at X-ray Service from La Laguna University (SIDIX). CrysAlisPro [38] software was used to collect, index, scale and apply analytical absorption correction based on faces of the crystal. Structure solution was obtained by direct methods, using the SIR2011 [39] software and Fourier recycling and least-squares refinement were used for the model completion with SHELXL-2014 [40]. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms have been placed in geometrically suitable positions and refined riding with isotropic thermal parameter related to the equivalent isotropic thermal parameter of the parent atom. The methyl-H atoms were refined as rigid groups, which were allowed to rotate but not to tip, with $U_{iso}(H) = 1.5U_{eq}(C)$ and the other hydrogen atoms were allowed to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. Graphics were generated using Olex2 [41] program. Crystal data, collection procedures and refinement results are summarized in Table 1 where selected bonds lengths and angles are listed in Table 2.

Crystallographic data for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data Centre with reference number 989086. Copies of the data can be obtained free of charge on application to the CCDC, Cambridge, U.K. (http://www.ccdc.cam.ac.uk/).

T a b l e 1

Crystallographic data for [CuI(3-methyl-2-phenylpyridine)$_2$]

Compound	**I**	Space group	*Pna*2$_1$
Empirical formula	$C_{24}H_{22}N_2CuI$	*Z*	4
Formula weight	528.87	μ(MoK_α), mm^{-1}	2.370
Crystal system	Orthorhombic	Reflections	7667
a, *b*, *c*, Å	17.7336(11), 9.7843(5), 12.8783(8)	Unique / R_{int}	4340 / 0.0347
α, β, γ, deg.	90, 90, 90	*R*1[a] / *wR*2[b]	*R*1 = 0.0398, *wR*2 = 0.1059
V, Å^3	2234.5(2)	Residual ρ, e/Å^{-3}	0.64 and –0.73
T, K	295(2)		

[a] $R1 = \sum||F_0| - |F_c|| / \sum F_0$.

[b] $wR2 = [\sum[w(F_0^2 - F_c^2)^2] / \sum[w(F_0^2)^2]]^{1/2}$.

Table 2

Selected bond distances (Å) *and angles* (deg.) *for* [CuI(3-methyl-2-phenylpyridine)$_2$]

I1—Cu1	2.5507(9)	I1—Cu1—N1A	111.6(2)	C1B—N1B—C5B	118.3(7)
Cu1—N1A	1.984(7)	I1—Cu1—N1B	113.28(19)	N1A—C1A—C2A	122.5(10)
Cu1—N1B	1.982(7)	N1A—Cu1—N1B	135.1(3)	N1B—C1B—C2B	122.3(9)
N1A—C1A	1.349(12)	Cu1—N1A—C1A	120.7(6)	N1A—C5A—C4A	121.3(8)
N1A—C5A	1.367(11)	Cu1—N1A—C5A	121.1(6)	N1A—C5A—C6A	113.8(7)
N1B—C1B	1.341(11)	C1A—N1A—C5A	118.2(8)	N1B—C5B—C4B	122.7(8)
N1B—C5B	1.349(10)	Cu1—N1B—C1B	118.1(5)	N1B—C5B—C6B	114.6(7)
		Cu1—N1B—C5B	123.6(6)		

RESULTS AND DISCUSSION

Synthesis of the complex. The synthetic procedure for the preparation of the copper(I) complex is straightforward and involves mixing together an equimolar amount of CuI with the N-donor ligand in acetonitrile and stirring the reaction for 3 hours 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 (I) and no oxidation was observed during the synthetic procedure. However, in related synthesis when chloride or bromide are used as halides a colour change to green indicating the oxidation of Cu(I) to Cu(II) was experienced. We have observed that in the preparation of copper(I) halides complexes the structure is highly affected by the solvent used and by the ratio metal:ligand and a rich structural diversity is obtained when varying these factors. Therefore, mononuclear copper(I) complexes are favoured when coordinating solvents such as acetonitrile is used while polymeric structures are being obtained by using other non-coordinating solvents.

Crystal structure. The main crystal data and structure refinement parameters have been summarized in Table 1 while selected bonds and angles are depicted in Table 2. The compound [CuI(3-methyl-2-phenylpyridine)$_2$] (Fig. 1) is a three-coordinate metal complex. The copper (I) is surrounded by two N-donor atoms of the 3-methyl-2-phenylpyridine ligand and by one iodide ligand. The copper(I) environment exhibits a distorted trigonal planar coordination. The bond distances Cu1—N1A and Cu1—N1B are 1.984(7) Å and 1.982(7) Å, respectively, while the distance Cu1—I1 is 2.5507(9) Å. These distances are within the range of those reported for other related structures [13], [42, 43]. Bond angles for I1—Cu1—N1A and for I1—Cu1—N1B are 111,6(2)° and 113,3(19°, respectively

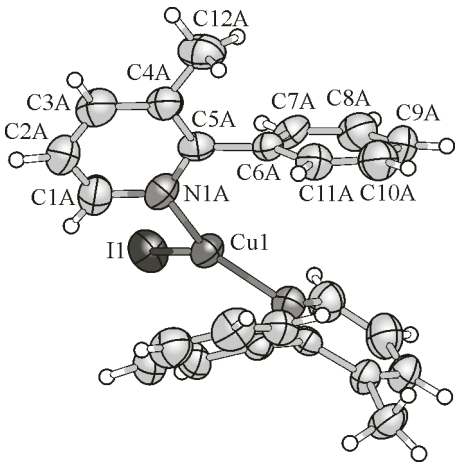


Fig. 1. View of the molecular structure of the complex [CuI(3-methyl-2-phenylpyridine)$_2$]

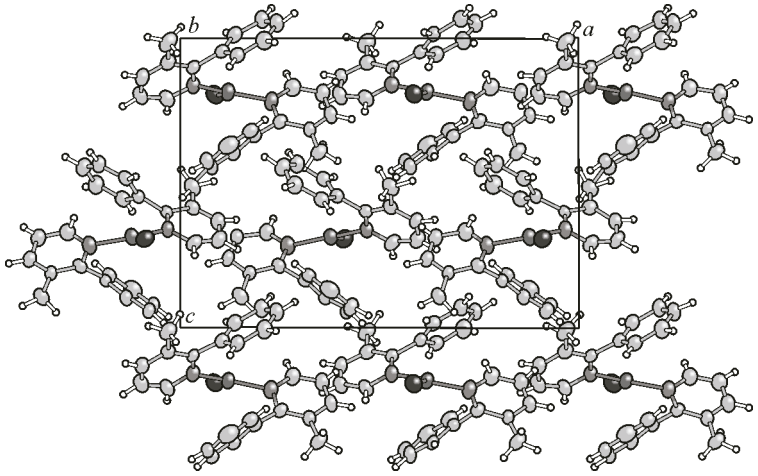


Fig. 2. Drawing showing the packing of [CuI(3-methyl-2-phenylpyridine)$_2$]

and the bond angle N1A—Cu1—N1B is 135.1(3) Å. The deviation of these values of the ideal 120° corresponding to a perfect trigonal planar geometry indicates a distorted trigonal planar geometry.

The compound contains two organic ligands of 3-methyl-2-phenylpyridine that we have labelled as molecule *A* and *B*. Both molecules are characterized by two rings, N1A, C1A, C2A, C3A, C4A, C5A (Ring1 with centroid Cg1) and C6A, C7A, C8A, C9A, C10A (Ring2 with centroid Cg3) and the same for molecule B, N1B, C1B, C2B, C3B, C4B, C5B (Ring3 with centroid Cg2) and C6B, C7B, C8B, C9B, C10B (Ring4 centroid Cg4). The angles between rings 1 and 3 (molecule *A*) and 2 and 4 (molecule *B*) are 63.7(5)° and 56.0(5)° respectively, while the angle formed between the rings 1 and is of 80.7(5)° which is close to perpendicular. The packing between molecules *A* and *B* is nearly parallel with angles of 38.3(5)° between rings 1 and 4 and 29.7(5)° between rings 2 and 3. This induces a weak π—π intramolecular interactions where the distances are 4.224(6) Å for Cg2…Cg3 and 4.458(6) Å for Cg1…Cg4. Also the compound presents a very week π-ring intermolecular interaction C—X…Cg where the distance of C…Cg is 3.553(12) Å (C8A…$Cg2^{i}$ ($i = -x, -y, 1/2+z$)).

Ackowledgements. R.H.M. thanks the Spanish Ministerio de Economía y Competitividad through Projects CTQ2012-37821-C02-01 and SAF2012-37344-C03-01. JGP thanks to the Ministerio Español de Ciencia e Innovación for fundings through Project MAT2010-21270-C04-02, MALTA Consolider CSD2007-0045. We are also grateful to the Servicios Generales of the Universidad de La Laguna for proving us with X-Ray facilities, elemental analyses and infrared spectroscopy.

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