

КРАТКИЕ СООБЩЕНИЯ

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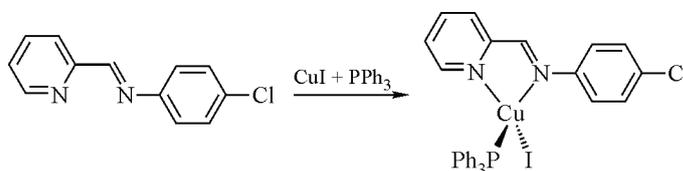
CRYSTAL STRUCTURE OF THE COPPER(I) COMPLEX $\text{Cu}(\text{py-Clan})(\text{PPh}_3)\text{I}$ A. D. Khalaji¹, K. Jafari², K. Fejfarova³, M. Dusek³¹Department of Chemistry, Golestan University, Faculty of Science, Gorgan, Iran
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A mixed ligand copper(I) Schiff base complex $[\text{Cu}(\text{py-Clan})(\text{PPh}_3)\text{I}]$, where py-Clan = 4-chlorophenylpyridine-2-ylmethylethylamine, is synthesized and structurally characterized by single crystal X-ray crystallography. In this complex, the copper(I) ion is in a distorted four-coordinate tetrahedral geometry. The Schiff base py-Clan ligand acts as a chelating ligand and coordinates to the copper center via two nitrogen atoms. The $[\text{Cu}(\text{py-Clan})(\text{PPh}_3)\text{I}]$ complex crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters: $a = 10.3339(12)$, $b = 34.524$, $c = 8.3940 \text{ \AA}$, $\beta = 114.759(8)^\circ$, $V = 2719.4(5) \text{ \AA}^3$ and $Z = 4$.

Key words: copper(I) complex, Schiff base, synthesis, crystal structure, tetrahedral.

The coordination chemistry of copper(I) complexes with bidentate diimine ligands, such as bipyridine and phenantroline, has received much attention over the last decades due to the potential application of these complexes in catalytic processes [1–3], photochromism and electrochemical properties [4, 5], the design of coordination polymers [6, 7], metallosupramolecular cylinder [8], and grid complexes [9]. Most of the studies have been made on tetrahedral copper(I) complexes of the $[\text{Cu}(\text{LL})_2]^+$ type where LL is a diimine Schiff base [10, 11]. Although reports on copper(I) complexes are numerous, limited works were performed on mixed ligand copper(I) complexes of the $[\text{Cu}(\text{LL})\text{PX}]$ type ($X = \text{Cl}, \text{Br}, \text{I}$) [12, 13]. This study is a part of our ongoing effort to synthesize and characterize copper(I) complexes with a bidentate Schiff base ligand [6, 7, 13]. Herein, we report the synthesis and crystal structure of the mixed ligand copper(I) complex $[\text{Cu}(\text{py-Clan})(\text{PPh}_3)\text{I}]$ (Scheme 1).



Scheme 1. Synthesis and chemical structure of the ligand and its copper(I) complex

Experimental. All reagents and solvents for the synthesis and analysis were commercially available and used as received without further purifications. Infrared spectra were recorded using KBr disks on a FT-IR Perkin—Elmer spectrophotometer. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer.

Preparation of 4-chlorophenylpyridine-2-ylmethyleneamine (py-Clan). A solution of pyridine-2-carbaldehyde (1.07 g, 0.01 mol) in 25 ml diethylether was added to a solution of 4-chloroaniline (1.28 g, 0.01 mol) in 10 ml diethylether and stirred for 30 min. The py-Clan ligand was obtained as white microcrystalline powder. Yield: 88 %. Anal. calcd. for $C_{12}H_9N_2Cl$ (%): C 66.52, H 4.19, N 12.93; found C 66.65, H 4.26, N 13.01.

Preparation of [Cu(py-Clan)(PPh₃)I]. 0.190 g (1 mmol) CuI was dissolved in acetonitrile (10 ml) and a solution of PPh₃ (0.262 g, 1 mmol) in acetonitrile (5 ml) was added to it dropwise. The mixture was stirred for 10 min and then 146 mg (1 mmol) of py-Clan in 5 ml acetonitrile were added and stirred for an additional 10 min. Slow evaporation of the solvent at room temperature gave title compound (**1**) as dark red crystals after about 4 days. The crystals were collected by filtration and dried at room temperature for 3 days. Yield: 76 %. Anal. calcd. for $C_{30}H_{24}ClCuIN_2P$ (%): C 53.83, H 3.61, N 4.18; found C 53.79, H 3.68, N 4.12.

X-ray structure determination. A single crystal of [Cu(py-Clan)(PPh₃)I] was chosen for X-Ray diffraction study. Crystallographic measurements were performed at room temperature with a four circle CCD Gemini (Oxford Ltd.) diffractometer using MoK α radiation ($\lambda = 1.5418 \text{ \AA}$), a sealed X-ray tube collimated by mirrors and an Atlas CCD detector. The crystal structure was solved by direct methods with the SIR2002 program [14] and refined with the Jana2006 program package [15] by the full-matrix least-squares technique on F^2 . The molecular structure plots were prepared by ORTEP III [16]. Hydrogen atoms were mostly discernible in difference Fourier maps and could be refined to reasonable geometry. According to common practice, they were nevertheless kept in ideal positions during the refinement. The isotropic atomic displacement parameters of hydrogen atoms were evaluated as $1.2U_{eq}$ of the parent atom. Crystal data and details of the experiment: $T = 120 \text{ K}$, $a = 10.3339(12)$, $b = 34.524(2)$, $c = 8.3940(9) \text{ \AA}$, $\beta = 114.759(8)^\circ$, $V = 2719.4(5) \text{ \AA}^3$, $P2_1/c$, $Z = 4$, $\mu = 11.67 \text{ mm}^{-1}$, $R_{int} = 0.056$, $F_{000} = 1328$, $R[F^2 > 2\sigma(F^2)] = 0.052$, $wR(F^2) = 0.133$, $S = 1.62$, reflections with $I > 3\sigma(I) = 3792$, independent reflections 4702, measured reflections 12418.

Results and discussion. The molecular structure including the atom numbering scheme is shown in Fig. 1, *a*. The selected bond lengths and angles are listed in Table 1. The [Cu(py-Clan)(PPh₃)I] complex crystallizes in the monoclinic system with the space group $P2_1/c$. The copper(I) ion in [Cu(py-Clan)(PPh₃)I] is tetrahedrally coordinated by two N atoms of the Schiff base ligand, one P atom from triphenylphosphine, and one iodide atom. The coordination around the copper(I) ion is considerably distorted due to the restricting bite angle of the chelating Schiff base ligand. The N(1)—Cu(1)—N(2) angle is only $79.3(2)^\circ$ in [Cu(py-Clan)(PPh₃)I], being below the usual range of $82\text{--}90^\circ$

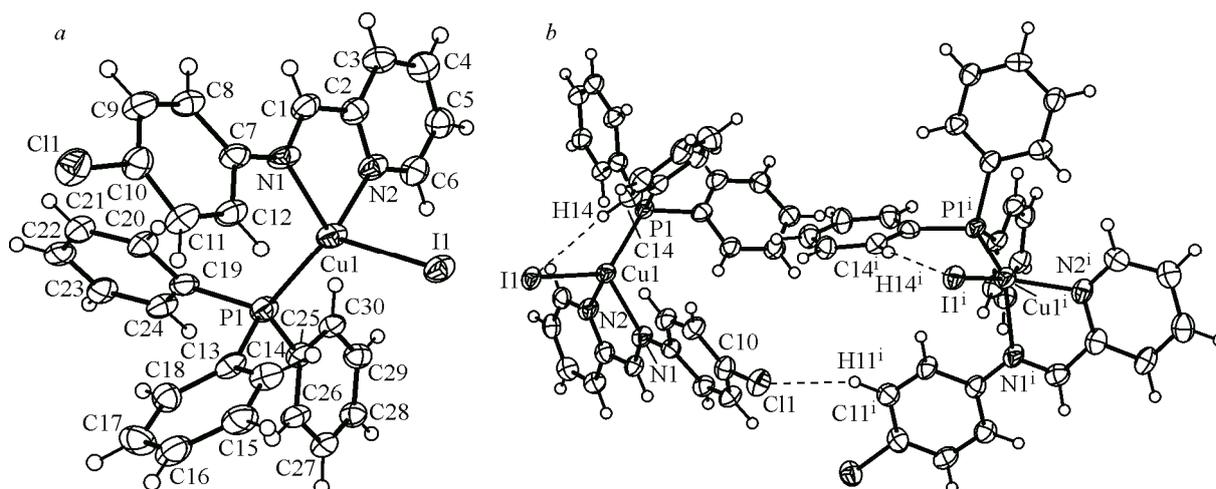


Fig. 1. An ORTEP view of [Cu(py-Clan)(PPh₃)I]. Ellipsoids are drawn at the 50 % probability level (*a*). Part of the crystal structure of [Cu(py-Clan)(PPh₃)I] showing inter- and intra-molecular hydrogen bonds (*b*)

Table 1

Selected bond geometric parameters (Å, deg.)

I1—Cu1	2.6126(11)	I1—Cu1—P1	115.11(6)	I1—Cu1—N1	105.51(11)
Cu1—N1	2.143(6)	I1—Cu1—N2	103.11(13)	P1—Cu1—N1	118.60(15)
N1—C1	1.278(9)	P1—Cu1—N2	128.75(15)	N1—Cu1—N2	79.3(2)
N2—C2	1.378(11)	Cu1—N1—C1	113.3(5)	Cu1—N1—C7	126.0(5)
Cu1—P1	2.218(2)	C1—N1—C7	120.5(7)	Cu1—N2—C2	111.8(4)
Cu1—N2	2.092(6)	Cu1—N2—C6	129.7(6)	C2—N2—C6	118.4(6)
N1—C7	1.421(9)				
N2—C6	1.324(9)				

found for other similar copper(I) complexes [17–21]. On the contrary, the I(1)—Cu(1)—P(1), P(1)—Cu(1)—N(1) and P(1)—Cu(1)—N(2) bond angles are much larger than those of tetrahedral complexes due to the steric effects from the bulky triphenylphosphine group [12, 13]. The average of Cu—N (2.43 Å) and Cu—I (2.67 Å) bond lengths in [Cu(py-Clan)(PPh₃)I] agrees well with the corresponding values in other mixed ligand copper(I) complexes [12, 13, 17–21]. Different to the stacking manners of two neighboring Schiff base py-Clan ligands in [Cu(py-Clan)(PPh₃)I], the non-classical intermolecular hydrogen bond of the C(11)—H(11)···Cl(1) type (3.648 Å, 148.928°) occurs only between the two adjacent Schiff base ligands. Also, a weak non-classical intramolecular hydrogen bond of the C(14)—H(14)···I(1) type (3.902 Å, 165.162°) exists in [Cu(py-Clan)(PPh₃)I] (Fig. 1, b).

In the [Cu(py-Clan)(PPh₃)I] complex, the Schiff base py-Clan ligand acts as a bidentate chelate ligand through one nitrogen atom from the pyridine ring and one nitrogen atom from the iminic group. Despite the fact that the donor iminic nitrogen atom is *sp*² hybridized, some strain in the chelate ring is suggested by a deviation from the 120° angle about the iminic nitrogen atom [12, 13, 17–21]. This deviation is reflected by the C(1)—N(1)—C(7) angle being 126.0(5)° in **1**.

Supplementary data. Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC No. 910761. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>.

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