# Copper(II) complexes with 3-(2-pyridyl)-4,5-dihydro-1*H*-pyrazoles: synthesis, structural and electrochemical studies

N. I. Vorozhtsov, A. G. Majouga, E. K. Beloglazkina,\* A. A. Moiseeva, G. A. Golubeva, I. V. Evstaf ev, L. A. Sviridova, and N. V. Zyk

> Department of Chemistry, M. V. Lomonosov Moscow State University, 1 Leninskie Gory, 119991 Moscow, Russian Federation. E-mail: bel@org.chem.msu.ru

Three new copper(II) complexes with the 3-(2-pyridyl)-4,5-dihydro-1*H*-pyrazole ligands were obtained by reactions of appropriate organic ligands with  $CuCl_2 \cdot 2H_2O$ . The structures of the complexes were determined by X-ray diffraction. The molecular formula of all the complexes can be written as  $2(L \cdot MCl_2)$  (L is an organic ligand). The coordination polyhedron of either copper ion is a distorted trigonal bipyramid made up of two N atoms (coming from the pyrazoline and pyridine rings) and one axial and two bridging chloride anions. The electrochemical behavior of 1,5-diphenyl-3-(2-pyridyl)-4,5-dihydro-1*H*-pyrazole and its Cu<sup>II</sup> complex was studied by cyclic voltammetry; the mechanisms of their electrooxidation and electroreduction were proposed.

**Key words:** 3-(2-pyridyl)-4,5-dihydro-1*H*-pyrazoles, copper(1) complexes, X-ray diffraction, cyclic voltammetry.

Dinuclear complexes of transition metals are attractive for researchers because of their growing interest in compounds containing closely spaced metal centers magnetically interacting with each other.<sup>1–3</sup> Being crucial for the functions performed by dinuclear copper-containing enzymes, such interactions give impetus to investigations of low-molecular-weight analogs of metalloproteins capable of promoting various redox reactions, including activation of molecular oxygen.<sup>4–8</sup>

According to the criteria formulated earlier,<sup>9</sup> dinuclear metal complexes can form if (1) the coordination sphere of a metal is incompletely filled with electron-donating groups of a polydentate organic ligand and (2) either an organic ligand or an additional inorganic anion contains electron-donating atoms capable of bridging metal centers. From this viewpoint, reactions of organic N,N'-type bidentate ligands (bipyridyl analogs) with metal chlorides are promising for the synthesis of dinuclear complexes.

3-(2-Pyridyl)-4,5-dihydro-1*H*-pyrazoles are heterocyclic N,N´-type ligands that potentially can form mono-, di-, and polynuclear complexes with transition metals. However, complexation reactions of 2-pyrazoline derivatives have remained poorly studied until recently. Structurally characterized complexes with such ligands include only two documented examples: a mononuclear ruthenium(II) complex<sup>9</sup> and a dinuclear zinc(II) complex.<sup>10</sup> Organic ligands of the 3-(2-pyridyl)-4,5-dihydro-1*H*pyrazole series can be employed as selective fluorescent sensors for Zn<sup>II</sup> ions.<sup>11</sup> At the same time, Ni<sup>II</sup>, Co<sup>II</sup>, and Cu<sup>II</sup> complexes with pyridylpyrazolines have not been isolated in the individual state, yet being detected by electronic absorption spectroscopy.<sup>11</sup>

The goal of the present work was to obtain and structurally characterize dinuclear Cu<sup>II</sup> complexes with 3-(2pyridyl)-4,5-dihydro-1*H*-pyrazoles and study their electrochemical behavior.

## **Results and Discussion**

1,5-Disubstituted 3-(2-pyridyl)-4,5-dihydro-1*H*-pyrazoles **1** and **2** were obtained from appropriate chalcones according to a modified procedure<sup>12</sup> (Scheme 1).

# Scheme 1



 $Ar = Ph(1), 4-MeOC_6H_4(2)$ 

Reagents: PhNH<sub>2</sub>NH<sub>2</sub>, NaOH, EtOH.

3,5-Disubstituted 1-benzylpyrazoline **3** was synthesized as described earlier<sup>13</sup> (Scheme 2).

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#### Scheme 2



Reagents: *i*. 1) NH<sub>2</sub>NH<sub>2</sub>·H<sub>2</sub>O, 2) AcOH; *ii*. 1) HBF<sub>4</sub>, 2) PhCHO; *iii*. 1)NaBH<sub>4</sub>, EtOH, 2) HCl, H<sub>2</sub>O.

Compounds 1-3 were used as ligands in complexation reactions with copper(11) salt. For this purpose, a solution of CuCl<sub>2</sub> in MeOH was made to slowly diffuse into solutions of organic ligands 1-3 in CH<sub>2</sub>Cl<sub>2</sub>. The resulting complexes 4-6 (Scheme 3) were examined by elemental analysis, electronic absorption spectroscopy, and X-ray diffraction.

In the UV-Vis spectra of complexes 5 and 6, the absorption peaks at 320–380 nm are slightly shifted, and their optical density is considerably increased, compared to the spectra of the starting ligands 2 and 3. These peaks have been attributed<sup>11</sup> to the  $\pi$ - $\pi$ \*-transitions in the organic ligand and are characteristic of complexes with a metal : ligand ratio of 1 : 1. The spectra do not show absorption bands at 400–600 nm that would be indicative of the formation of complexes ML<sub>2</sub> in solution.<sup>11</sup>

X-ray diffraction study of complexes 4–6. Structures 4–6 were confirmed by X-ray diffraction (Fig. 1). These complexes are dinuclear clusters of the formula  $Cu_2L_2Cl_4$  (L = 1–3). Crystallographic parameters and the data collection and refinement statistics for complexes 4–6 are summarized in Table 1. Selected bond lengths and bond angles in these structures are given in Table 2. According to the X-ray diffraction data, the coordination polyhedron of either copper atom in complexes 4–6 is a distorted





Reagents: CuCl<sub>2</sub>·H<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, MeOH.

trigonal bipyramid made up of two N atoms of the pyrazoline and pyridine rings and one axial and two bridging chloride anions. The copper—copper distance ( $\sim$ 3.3 Å) is longer than the double van der Waals radius of the Cu atom, thus suggesting that the metal ions do not interact directly in the crystal structures of these complexes.

Electrochemical study of ligand 1 and its complex 4. Ligand 1 and dinuclear copper(II) complex 4 were studied



Fig. 1. The molecular structures of complexes 4 (*a*), 5 (*b*), and 6 (*c*) (X-ray diffraction data).

Parameter	4	5	6
Molecular formula	C <sub>40</sub> H <sub>40</sub> Cl <sub>4</sub> Cu <sub>2</sub> N <sub>6</sub>	$C_{42}H_{38}C_{14}Cu_2N_6O_2$	C42H38Cl4Cu2N6
Molecular weight	873.66	927.66	895.68
Space group	P21/c	$P\overline{1}$	<i>P</i> 21/ <i>c</i>
a/Å	14.900(10)	9.8740(9)	15.5750(19)
b/Å	7.467(6)	9.9050(9)	8.7391(8)
c/Å	16.096(6)	12.2010(11)	15.994(2)
α/deg	90.00	87.120(10)	90.00
β/deg	94.77(5)	89.470(10)	108.107(9)
γ/deg	90.00	60.530(10)	90.00
$V/Å^3$	1784.6(19)	1037.41	2069.16
Z	2	1	2
$d_{\rm calc}/{ m g~cm^{-3}}$	1.626	1.485	1.438
$\mu/mm^{-1}$	1.532	1.327	1.324
<i>F</i> (000)	896	474	916
$\theta$ scan range/deg	2.3-23.7	2.37-26.00	2.60-17.09
Ranges of $h, k, l$	$-20 \le h \le 20,$	$-8 \le h \le 12$	$-19 \le h \le 18$
	$-10 \le k \le 10,$	$-12 \le k \le 11,$	$-3 \le k \le 10,$
	$-21 \le l \le 21$	$-14 \le l \le 15$	$-19 \le l \le 19$
Number of measured/unique reflections	4727/3526	3932/707	4047/1678
Number of refined parameters	235	245	209
GOOF on $F^2$	1.505	0.586	0.847
R factors $(I \ge 2\sigma(I))$			
$R_1$	0.0530	0.0591	0.0661
$wR_2$	0.1212	0.0999	0.1439
<i>R</i> factors (for all reflections)			
$R_1$	0.0775	0.2702	031634
$wR_2$	0.1317	0.1398	0.1857

Table 1. Crystallographic parameters and the data collection and refinement statistics for complexes 4-6

by cyclic voltammetry (CV) at a glassy carbon electrode in DMF with 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> in DMF as a supporting electrolyte. Ligand 1 is reduced in two steps and is oxidized in a single step. The first redox peaks correspond to one-electron transfer (Table 3, Fig. 2), which becomes evident when comparing the heights of these peaks with

Table 2. Selected bond lengths and bond angles in complexes 4–6

Parameter	4	5	6
Bond	d∕Å		
Cu(1)-Cl(1)	2.2307(15)	2.209(3)	2.224(2)
Cu(1)-Cl(2)	2.2882(14)	2.279(3)	2.288(2)
Cu(1)-Cl(2)	2.6184(17)	2.327(3)	2.648(2)
Cu(1) - N(1)	2.088(3)	2.000(8)	2.038(6)
Cu(1) - N(2)	2.041(3)	2.52(1)	2.048(5)
Bond angle	ω/deg		
N(1) - Cu(1) - N(2)	78.66(12)	74.2(4)	78.9(2)
N(1) - Cu(1) - Cl(1)	91.08(9)	93.4(3)	93.49(18)
N(2) - Cu(1) - Cl(2)	92.37(9)	87.4(3)	93.24(8)
Cl(1) - Cu(1) - Cl(2)	93.60(6)	84.70(9)	90.18(7)
Cu(1)-Cl(2)-Cu(1)	90.63(5)	95.30(9)	89.82(7)



**Fig. 2.** The frontier orbitals of ligand **1** from quantum chemical computations at the PM3 level: (*a*) HOMO and (*b*) LUMO.

**Table 3.** The oxidation  $(E^{Ox})$  and reduction potentials  $(E^{Red})$  of ligand 1 and its complex  $4^a$ 

Compound	$E_{\rm p}^{\rm Red}$	$E_{\rm p}^{\rm Ox}$
1	-2.03 (-1.98),-0.70;	1.01
4	$\begin{array}{c} -2.56 \ (-0.70), \ -0.17 \\ 0.37 \ (0.50)^b; \\ -2.00 \ (-1.95); \ -2.27 \end{array}$	0.98 <sup>b</sup> ; 1.16

<sup>*a*</sup> DMF, glassy carbon electrode. The peak potentials on the reverse scan are given in parentheses.

<sup>b</sup> The initial potential is 0.7 V.

the heights of the peaks for one-electron oxidation of ferrocene used in equal concentration. The results of semiempirical (PM3)<sup>14</sup> quantum chemical calculations (see Fig. 2) suggest that the HOMO is mainly contributed by the conjugated  $\pi$ -system of the phenylpyrazoline fragment (this system is most liable to oxidation in the molecule) and that the LUMO is mainly contributed by the  $\pi$ -system consisting of the C=N bond of the pyrazoline ring and the pyridine fragment (this system will accept an electron in the first reduction step; it should be noted that the first reduction potential is close to the reduction potential of pyridine<sup>15</sup> ( $E_{pc}$ = -2.07 V)).

In contrast to the CV curve of free ligand 1, that of dinuclear complex 4 shows a quasireversible reduction peak



**Fig. 3.** Cyclic voltammograms ( $C = 10^{-3} \text{ mol } L^{-1}$ , glassy carbon electrode, DMF, 0.1 *M* Bu<sub>4</sub>NClO<sub>4</sub>) of ligand 1 (*a*) and complex 4 (*b*).

at 0.37/0.50 V (see Table 3, Fig. 3) due to the transition  $Cu^{II} \rightarrow Cu^{I}$ . Both the copper ions of the dinuclear complex are simultaneously reduced at the same potential; hence, they do not interact with each other. The copper(1)-containing intermediate is stable on the CV time scale and undergoes no disproportionation into  $Cu^{II}$  and  $Cu^{0}$  complexes. This is confirmed by the reverse scan (down to  $E_{pc} \approx -2.0$  V) revealing no peak due to the oxidative desorption of metallic copper from the electrode surface (see Fig. 3). Since the potential of the second cathodic peak of complex **4** is close to the reduction potential of the free ligand, further reduction of the complex seems to occur at the pyrazolylpyridine fragment. Therefore, we can propose a sequential scheme for the first two reduction steps of complex **4** (Scheme 4).

### Scheme 4

$$(Cu^{II}L)_2 \xrightarrow{+2 e^-} (Cu^{I}L)_2 \xrightarrow{+2 e^-} (Cu^{I}L^-)_2$$

In contrast to free ligand 1, the CV curve of complex 4 shows an additional oxidation peak at  $E_{pa} = 1.16$  V corresponding to the oxidation of coordinated chloride anions.

To sum up, we demonstrated that the 3-(2-pyridyl)-4,5-dihydro-1*H*-pyrazoles react with cupric chloride to give dinuclear complexes that are stable in both the crystalline state and in solution. The results of the electrochemical study of a dinuclear copper complex with 1,5-diphenyl-3-(2-pyridyl)-4,5-dihydro-1*H*-pyrazole suggest the independent reduction of either metal center in this complex as well as the stability of its reduced form in DMF.

## **Experimental**

The course of the reactions was monitored and the reaction products were identified by TLC on Silufol plates. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance instrument (400 MHz). IR spectra were recorded on UR-20 instruments (Nujol). UV-Vis spectra were recorded on a Specord instrument in EtOH. X-ray diffraction studies were performed on a STOE STADI VARI Pilatus-100K diffractometer (Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å, T = 295(2) K) purchased in conformity with the development plan of the M. V. Lomonosov Moscow State University.

Cyclic voltammograms were recorded using a PI-50-1.1 potentiostat connected to a PR-8 programmer. The potentials of the working electrode (glassy carbon disk, d = 2 mm) were measured versus Ag/AgCl/KCl(sat.) as a reference electrode; 0.1 *M* Bu<sub>4</sub>NClO<sub>4</sub> in DMF was employed as a supporting electrolyte. A platinum plate served as an auxiliary electrode. Prior to the measurements, the working electrodes were polished with powdered alumina (particle size <10 µm, Sigma-Aldrich). The potential scan rate was 200 mV s<sup>-1</sup>. The potentials are corrected for *iR*-compensation. For all measurements, dry argon and deaerated solvents were used.

Pyridyl-containing chalcones for the synthesis of compounds 1-3 were prepared according to a modified procedure.<sup>16</sup>

**1,5-Diphenyl-3-(2-pyridyl)-4,5-dihydro-1***H***-pyrazole (1).** A solution of phenylhydrazine (0.74 g, 6.8 mmol) in EtOH (10 mL) was added to a suspension of NaOH (0.27 g) in EtOH (20 mL). The mixture was stirred for 5 min. Then 3-phenyl-1-(2-pyridyl)prop-2-en-1-one (1.44 g, 6.8 mmol) was added for 10 min. The reaction mixture was stirred for 30 min. The yellow precipitate that formed was washed with cold EtOH and recrystallized from aqueous EtOH (1:1). The yield of compound 1 was 1.4 g (70%), m.p. 114–116 °C (*cf.* Ref. 12: m.p. 115–117 °C).

**5-(4-Methoxyphenyl)-1-phenyl-3-(2-pyridyl)-4,5-dihydro-1H-pyrazole (2)** was obtained from 3-(4-methoxyphenyl)-1-(2pyridyl)prop-2-en-1-one (2.39 g, 10 mmol) as described above for compound **1**. Yield 1.52 g (54%), m.p. 129 °C (*cf.* Ref. 12: m.p. 130 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>), 8: 3.32 (dd, 1 H, H(4),  $J_1$  = 12.0 Hz,  $J_2$  = 4.0 Hz); 3.80 (s, 3 H, OMe); 3.97 (dd, 1 H, H(4),  $J_1$  = 18.0 Hz,  $J_2$  = 12.0 Hz); 5.32–5.36 (m, 1 H, H(5)); 6.81–6.88 (m, 3 H, Ar); 7.12–7.29 (m, 7 H, Ar); 7.72 (m, 1 H, Ph); 8.16 (t, 1 H, H(3), pyridyl, J = 4.6 Hz); 8.56 (d, 1 H, H(6), pyridyl, J = 3.0 Hz). UV,  $\lambda$ /nm (lgɛ): 231 (3.63), 250 (3.56), 379 (3.42).

**1-Benzyl-5-phenyl-3-(2-pyridyl)-4,5-dihydro-1***H***-pyrazole (3).** A hot solution of 3-phenyl-1-(2-pyridyl)prop-2-en-1-one (4.18 g, 0.02 mol) in EtOH (13 mL) was added in portions at 50—60 °C to a solution of hydrazine hydrate (3 g, 0.02 mol) in EtOH (4.8 mL). After the formation of a precipitate, acetic acid (2.4 mL) was added dropwise and the reaction mixture was refluxed for 1.5 h. The resulting solution was cooled and the precipitate that formed was filtered off, washed with water, and squeezed. The yield of 5-phenyl-3-(2-pyridyl)-4,5-dihydro-1*H*-pyrazole was 3.57 g (80%). This compound was used in subsequent reactions without further purification because of its limited stability.

Tetrafluoroboric acid (50%, 1 mL) was added to a vigorously stirred solution of 5-phenyl-3-(2-pyridyl)-4,5-dihydro-1*H*-pyrazole (2.46 g, 0.011 mol) in  $CH_2Cl_2$  (25 mL). Then benzalde-hyde (2.02 g, 0.020 mol) was added dropwise with stirring. The reaction mixture was stirred for 6 h, washed with water to a neutral reaction, and evaporated to dryness. The yield of the benzylidene salt was 3.6 g (81%), dark brown crystals.

Sodium borohydride (0.57 g, 0.015 mol) was gradually added to a suspension of the benzylidene salt (1.00 g, 0.005 mol) in EtOH (20 mL). The reaction mixture was stirred at room temperature for 2 h, diluted with water (5 mL), acidified with HCl to pH 7, and concentrated. Water (20 mL) was added to the solid residue, and the product was extracted with chloroform. The organic extracts were washed with water and brine, dried with  $Na_2SO_4$ , and concentrated. The residue was chromatographed on a dry column ( $5 \times 40$  mm, SiO<sub>2</sub>) with benzene—ethyl acetate (20:1) as an eluent. A fraction with  $R_{\rm f}$  0.85 (benzene-ethyl acetate, 2:1) was collected. The yield of compound 3 was 0.5 g (50%), m.p. 102–104 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ: 3.10 (dd, 1 H,  $H(4), J_1 = 6.0 Hz, J_2 = 5.0 Hz$ ; 3.64 (dd, 1 H, H(4),  $J_1 = 6.0 Hz$ ,  $J_2 = 5.0$  Hz); 4.03 (d, 1 H, CH<sub>2</sub>Ph, J = 12.0 Hz); 4.39 (dd, 1 H,  $H(5), J_1 = 6.0 \text{ Hz}, J_2 = 5.0 \text{ Hz}); 4.62 (d, 1 \text{ H}, \text{CH}_2\text{Ph}, J = 12.0 \text{ Hz});$ 7.17 (m, 1 H, Ar); 7.20-7.45 (m, 10 H, Ar); 7.68 (t, 1 H, pyridyl, J = 3.5 Hz); 8.00 (d, 1 H, pyridyl, J = 5.0 Hz). IR, v/cm<sup>-1</sup>: 1570 (C=N). UV, λ/nm (lgε): 243 (4.92), 324 (3.84).

Synthesis of complexes from pyridylpyrazolines 1-3 and CuCl<sub>2</sub> (general procedure). Methanol (2 mL) was slowly added to a solution of pyridylpyrazoline 1-3 (1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) so that the mixture became separated in layers. A solution of CuCl<sub>2</sub>·2H<sub>2</sub>O (1 mmol) in MeOH (2 mL) was delivered to the interface by carefully pouring it down the wall of the reaction vessel. The resulting mixture was kept in the dark for precipitation. The black crystalline complex that formed was filtered off and dried in air.

**Di-µ-chloro-bis{chloro[1,5-diphenyl-3-(2-pyridyl)-4,5-di-hydro-1***H***-pyrazole]copper(** $\pi$ **)}** (4). Yield 0.28 g (65%), m.p. 236–240 °C. IR,  $\nu$ /cm<sup>-1</sup>: 1620 (C=N). Calculated (%): C, 55.31; H, 3.92; N, 9.68. C<sub>40</sub>H<sub>40</sub>Cl<sub>4</sub>Cu<sub>2</sub>N<sub>6</sub>. Found (%): C, 55.10; H, 3.91; N, 9.58.

**Di-μ-chloro-bis{chloro[5-(4-methoxyphenyl)-1-phenyl-3-(2-pyridyl)-4,5-dihydro-1***H***-pyrazole]copper(II)} (5).** Yield 0.34 g (72%), m.p. 205–210 °C. IR,  $\nu/cm^{-1}$ : 1610 (C=N). UV-Vis,  $\lambda/nm$  (lgε): 340 (4.65). Calculated (%): C, 54.38; H, 4.13; N, 9.06. C<sub>42</sub>H<sub>38</sub>Cl<sub>4</sub>Cu<sub>2</sub>N<sub>6</sub>O<sub>2</sub>. Found (%): C, 55.12; H, 4.08; N, 9.49.

**Bis**{[1-benzyl-5-phenyl-3-(2-pyridyl)-4,5-dihydro-1*H*-pyrazole]-μ-chloro-chlorocopper(π)} (6). Yield 0.23 g (53%), m.p. 253-255 °C. IR, v/cm<sup>-1</sup>: 1610 (C=N). UV-Vis,  $\lambda$ /nm (lgε): 231 (4.30), 379 (4.30). Calculated (%): C, 56.26; H, 4.24; N, 9.38. C<sub>42</sub>H<sub>38</sub>Cl<sub>4</sub>Cu<sub>2</sub>N<sub>6</sub>. Found (%): C, 56.01; H, 4.45; N, 9.30.

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