

Synthesis and Properties of Two New Cu(I) Complexes Based on 5,6-Substituted Imidazole-2,9-dimethyl-1,10-phenanthroline and Triphenylphosphine¹

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Abstract—Two new Cu(I) complexes, Cu(NPIP)(PPh₃)₂ (**1**) and Cu(MPIP)(PPh₃)₂ (**2**), (NHPIP: 2-(4-nitrophenyl) imidazole-2,9-dimethyl-1,10-phenanthroline; MHPIP: 2-(4-methylphenyl)imidazole-2,9-dimethyl-1,10-phenanthroline) have been synthesized and characterized by element analysis, IR and ¹H NMR spectra. TG experiments demonstrated that the complexes were stable up to ca 230°C indicating their high thermal stability. According to fluorescence spectra, the complexes exhibited yellow emission at 602 nm under excitation at 260 nm.

Keywords: Cu(I) complex, thermal stability, UV spectra, luminescence

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INTRODUCTION

Over recent years the design and synthesis of Cu(I) complexes attracted considerable attention not only due to accessibility and low toxicity of raw materials but also their potential applications as luminescent materials [1, 2]. 1, 10-Phenanthroline (1,10-phen) has been extensively used in constructing transition metal complexes with excellent luminescence properties based on its extended π -system and rigid structure [3, 4]. However, [Cu(1,10-phen)(PPh₃)₂] series exhibited weak luminescence because their tetrahedral geometry could distort the square planar geometry in solutions and accelerate nonradiative decay of the excited state [5, 6]. Introduction of a substituent in the 2,9-positions of 1,10-phen could prevent the flattening distortion [7]. So far, Cu(I) complexes containing 2,9-dialkyl-1,10-phen and phosphine mix ligands have been widely used in constructing photo- and electroactive devices [8, 9]. However, such types of Cu(I) complexes are primarily ionic ones and Cu(I) neutral complexes are rarely reported. 5,6-Substituted imidazole-1,10-phen ligand attracted our attention because they combine the versatile structural properties of imidazole (labile proton) and 1,10-phen (extended π -system). Lumine-

scence Cu(I) neutral complexes can be prepared by deprotonation of an N-donor ligand in alkaline media.

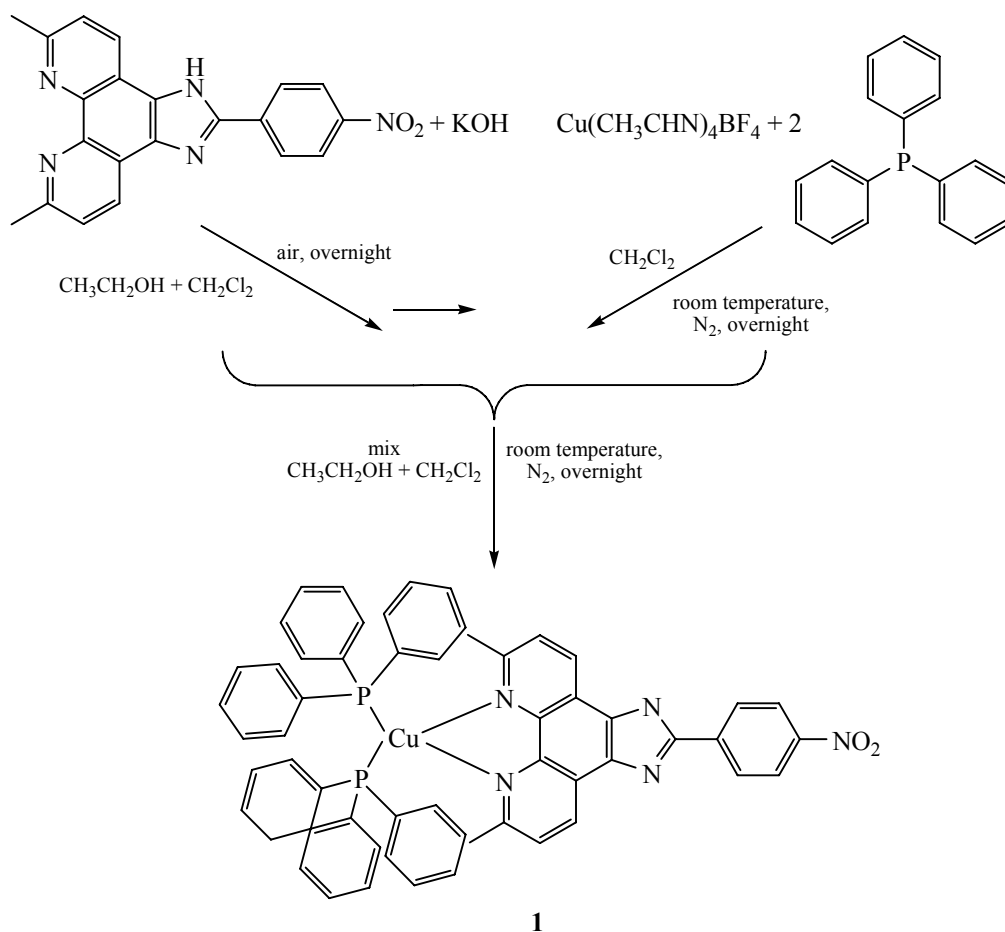
Here we report syntheses and characterizations of two Cu(I) neutral complexes containing deprotonated imidazole-1,10-phen ligands: NHPIP, 2-(4-nitro phenyl)-imidazole-2,9-dimethyl-1,10-phen, and MHPIP, 2-(4-methylphenyl) imidazole-2,9-dimethyl-1,10-phen and triphenylphosphine (PPh₃) ancillary ligand. Thermal stability, absorption and emission spectra of the complexes have been studied.

EXPERIMENTAL

The chemicals, including CuCl, PPh₃, 4-nitro benzaldehyde, 4-methyl benzaldehyde, 1,10-phen monohydrate, and fluoroboric acid (HBF₄), were obtained from commercial sources and used as received. NHPIP, MHPIP [10] and the reaction precursor [Cu(CH₃CN)₄]BF₄ [11] were prepared according to the known slightly modified procedures. All solvents were purified and distilled prior to use. The air sensitive manipulations were carried out under the nitrogen atmosphere using a standard Schlenk flask.

CHN elemental analysis was carried out using a Bio-Rad elemental analysis system. Absorption spectra were recorded on a TU-1901 UV-Vis spectrophotometer. ¹H NMR spectra (400 MHz) were measured on

¹ The text was submitted by the authors in English.

Scheme 1. Synthesis of Cu(NPIP)(PPh₃)₂ (**1**).

a Bruker ACF-400 spectrometer using DMSO as a solvent. PL spectra recorded on a RF-5301PC spectrofluorimeter connected to a photomultiplier tube with a xenon lamp as the excitation source.

Cu(NPIP)(PPh₃)₂ (1**).** A mixture of Cu(CH₃CN)₄BF₄ (0.064 g, 0.2 mmol) and PPh₃ (0.105 g, 0.4 mmol) in CH₂Cl₂ (10 mL) was stirred in a Schlenk flask under the nitrogen atmosphere for 5 h. The mixture of NPIP (0.074 g, 0.2 mmol) and KOH (0.012 g, 0.2 mmol) in CH₂Cl₂ (10 mL) and CH₃CH₂OH (10 mL) was stirred in a round bottom flask and upon the formation of a yellow solution transferred into a Schlenk flask by a syringe. The resulting mixture was stirred under the nitrogen atmosphere for 72 h at 35°C. The solvents were removed in a rotary evaporator and the residue was dissolved in diethyl ether. Yellow tiny crystals were obtained upon overnight storage (0.143 g, 75%). IR spectrum, ν , cm⁻¹: 3053 m, 2920 w, 1661 w, 1599 s, 1569 w, 1553 w, 1532 m, 1504 m, 1480 m, 1436 s, 1393 w, 1348 s, 1322 m, 1264 w,

1192 m, 1166 m, 1123 w, 1094 m, 1043 m, 1026 w, 998 w, 945 w, 825 m, 807 m, 743 s, 732 s, 695 s. ¹H NMR spectrum (CDCl₃), δ , ppm: 8.92 d ($J = 3.7$ Hz, 2H), 8.51 d.d ($J = 17.2, 6.7$ Hz, 2H), 8.15 d.d.d ($J = 42.9, 21.1, 8.1$ Hz, 2H), 7.69–7.56 m (2H), 7.37 d.d.d ($J = 38.9, 15.2, 7.5$ Hz, 12H), 7.21 s (2H), 7.06 d.d ($J = 37.3, 15.6$ Hz, 10H), 6.93 s (6H), 2.51 s (6H). Found, %: C 72.49; H 4.72; N 6.36. C₅₇H₄₄CuN₅O₂P₂. Calculated, %: C 71.54; H 4.60; N 6.28.

Cu(MPIP)(PPh₃)₂ (2**)** was synthesized from MPIP (0.068 g, 0.2 mmol) similarly to the procedure described above for **1**, yield 0.135 g (73%). IR spectrum, ν , cm⁻¹: 3056 w, 2338 w, 1965 w, 1819 w, 1609 m, 1585 m, 1563 w, 1511 m, 1480 m, 1460 m, 1434 m, 1347 m, 1295 w, 1247 m, 1214 m, 1173 m, 1093 m, 1059 s, 1024 s, 98 m, 957 m, 874 m, 831 m, 800 m, 741 s, 693 s, 669. ¹H NMR spectrum (CDCl₃), δ , ppm: 8.60 t ($J = 27.4$ Hz, 2H), 8.18 d ($J = 19.6$ Hz, 2H), 7.70–7.52 m (4H), 7.40 d ($J = 6.8$ Hz, 6H), 7.30 t ($J = 6.1$ Hz, 12H), 7.21 s (12H), 2.51 s (6H), 2.20 s (3H).

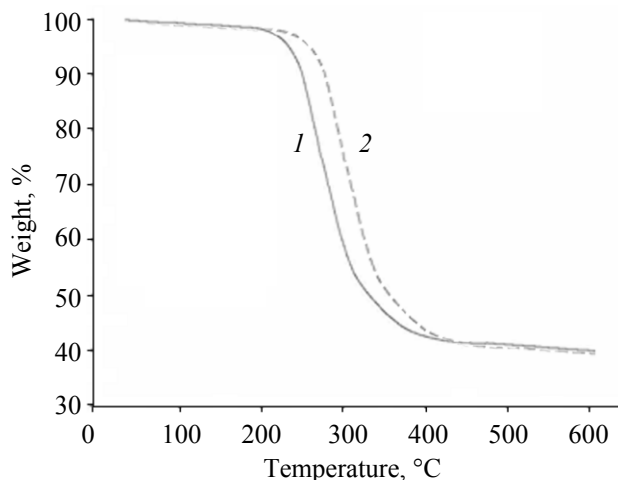


Fig. 1 TG curves of complexes (1) **1** and (2) **2**.

Found, %: C 70.71; H 4.92; N 5.87. $C_{58}H_{47}CuN_4P_2$.
Calculated, %: C 69.89; H 5.04; N 5.96.

RESULTS AND DISCUSSION

Syntheses and characterization. In the course of synthesis of complex **1** (Scheme 1) KOH reacted with N-donor ligand to form NPIP anion followed by its addition into the mixture of $Cu(CH_3CN)_4BF_4$ with PPh_3 . The side reaction of KOH with $Cu(CH_3CN)_4BF_4$ was retarded. KOH was found to be the most efficient in deprotonation of nitrogen containing ligand compared to NaOH due to better match of K^+ radius with that of BF_4^- .

1H NMR spectra of **1** and **2** confirmed the simultaneous coordination of N- and P-donor ligand. The disappearance of N–H signal of imidazole ring at ca. 14 ppm indicated deprotonation of the N-donor ligand.

Thermal analysis. According to TG analysis (Fig. 1) complexes **1** and **2** were stable in the range of 30 to ca. 230°C that makes these applicable in many areas.

Absorption spectra. In UV–Vis spectra the complex **2** demonstrated two intensive peaks at 242 and 270 nm and the complex **1** demonstrated an intensive peak at 235 nm and a weak shoulder peak at ca. 280 nm. According to the publication [12], the high-energy absorption peaks below 300 nm could be assigned to the ligand-to-ligand charge transfer (LLCT) and intraligand charge transition (ILCT).

Emission spectra. Emission spectra were measured at room temperature in different solvents under excita-

tion of 270 for **1** and 275 nm for **2**. No emission took place in CH_2Cl_2 , CH_3OH and anhydrous CH_3CN . However, weak to moderate yellow luminescence, $\lambda_{max} = 580$ nm for **1** and $\lambda_{max} = 598$ nm for **2**, was observed in anhydrous ether. According to the publication [13], the tendency of emission energies ($1 > 2$) is contrary to the electron donating ability of the N-donor ligand ($NPIP < MPIP$). The emission spectra of powder exhibited high emission intensity and similar emission, $\lambda_{max} = 584$ nm for **1** and 602 nm for **2**, with those of the solution emissions. The emission wavelength of **2**, 602 nm, was more red-shifted than that of **1** (584 nm). The red shift could be caused by introduction of the electron donating methyl group in the N-donor ligand, raising the LUMO level, less influencing the HOMO energy, thus decreasing the HOMO–LUMO gap [14].

CONCLUSIONS

We have synthesized two neutral mononuclear Cu(I) complexes bearing two different 1,10-phen-imidazole and PPh_3 ligands and determined the thermal stability of those.

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