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ARTICLE

Intramolecular electron transfer in Cu(II) complexes with aryl-imidazo-1,10-phenanthroline derivatives: experimental and quantum chemical calculation studies

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1H-imidazo[4,5-*f*][1,10]phenanthrolines containing phenyl- (**1**), 4-(N,N-dimethylamino)phenyl- (**2**), 4-(azadithiacrown-ether)phenyl- (**3**) 3,4-dimethoxyphenyl- (**4**) and 2,2'-bithiophen-5-yl- (**5**) were synthesized and their Cu(II) complexes were studied to determine the effect of substituent, geometry of complex and solvent nature on the spectral and redox properties of the copper complexes. It was found that in case of 4-(N,N-dimethylamino)phenyl- and 4-(azadithiacrown-ether)phenyl substituents the formation of $L_2{\cdot}Cu^{2+}$ complex of pseudo-tetrahedral geometry causes the appearance of an intense metal-to-ligand charge transfer (MLCT) band at the visible region and induces a positive shift in the reduction potential providing the occurrence of autoreduction of Cu(II). Density functional theory (DFT) and its extension to time dependent density functional theory (TD-DFT) were performed to study the molecular structure, electronic and spectroscopic properties of copper with the 4-(N,N-dimethylamino)phenyl-1H-imidazo[4,5-*f*][1,10]phenanthroline ligand (**2**). The calculation results are in agreement with those obtained from optical measurements. Electrochemical study showed that the autoreduction is observed when Cu^{2+}/Cu^{+} transfer and oxidation of ligand occur at the closed electrochemical condition.

Introduction

1H-imidazo[4,5-*f*][1,10]phenanthroline (abbreviated as IPh) as N-donor ligand possesses several interesting structural characteristics appropriate for coordination with different types of metal ions (Zn^{2+}, Mn^{2+} [1], Cd^{2+} [2], Co^{2+} [3], Pt^{2+} [4], lanthanides (III) (Ln = Eu, Dy, Er, Tb, Sm, Yb)[5], Ru^{2+} [6])). Also 1H-imidazo[4,5-*f*][1,10]phenanthrolines (IPh) are versatile chelating ligands employed in the design of DNA metallointercallators and photocleaving agents. [7–9]

The copper complexes constitute an important class of compounds from several point of view viz. bioinorganic, catalysis and magnetism.[10,11] Some groups synthesized a series of ionic and neutral Cu(I) complexes with diphosphine and IPh ligands.[12,13] Benisvy's group was obtained a square-like neutral *tetra*-Cu(II) complex using a similar dianionic IPh ligand through N,O-phenolate-imidazolate/N,N-phenanthroline coordinating sites.[14] In addition, IPh-Cu(II) complexes have been prepared to analyze the binding with DNA and their ability to cause DNA cleavage.[15]

Our research aimed the studying of autoreduction of Cu(II) in complex with IPh derivatives which has not been observed early. Copper(I) complexes with 2,9-dialkylphenanthroline or 6,6'- dialkyl-2,2'-bipyridine have been prepared via chemical[16] or photochemical reduction[17,18] of the corresponding copper(II) compounds. Autoreduction of bis-chelated copper(II) complexes of 6,6'-dialkyl- 2,2'-bipyridines[19] and 8-dimethylarsinoquinoline[20] has also been reported. In those papers, the reduction of copper(II) is not attributed to the donor atoms of ligands (that is, the electronic properties) but to the geometry of a complex, which is exclusively defined by the sterically hindered group of a ligand. Thus, upon the control of the geometry of a complex, which prefers Cu(I) to Cu(II), the reduction of copper(II) complexes to copper(I) complexes occurs.

The formation of copper(I) complexes upon interaction of copper(II) salts with organic sulfides, containing, as a rule, additional nitrogen donor atoms and representing tetradentate ligands has been also described. In most cases,

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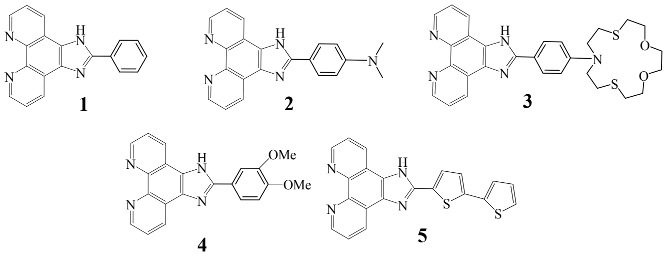
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x the oxidation product was not isolated but it might be assumed that during the reaction the one- electron oxidation of the thioether group by the Cu(II) ion occurs with the formation of the sulfur-centered radical-cation, which is further oxidized by the air oxygen or hydrolyzed to sulfoxide.[21, 22] The phenomenon is qualitatively attributed to the ability of the thioether donors to accept electron density into vacant 3d orbitals and stabilize the Cu(I) state.[23,24] Bis(benzimidazolyl)bis(thioether)copper chelates demonstrated reduction of the Cu(II) upon the irradiation with light.[25] The reaction proceeds *via* excitation of chelate complex, or eventually directly through LMCT reaction. Combination of azaheterocyclic residue and organic thioether or thiolate is similar to active centers of the most of mononuclear [26, 27] and binuclear[28] copper containing enzymes in which the metal atom is coordinated just by the donor sulfur atoms and nitrogen atoms (usually imidazole). Such copper containing enzymes (hemocyanins, thyrosinases, etc.) are capable to react with oxygen[29] and in the course of the reaction the exchange of electrons between the copper ion and the ligand occurs.

This manuscript concerns the reduction of Cu(II) to Cu(I) in complexes with IPh ligands containing phenyl- (**1**), 4-dimethylaminophenyl- (**2**), 4-(azadithiacrown-ether)phenyl- (**3**) 3,4-dimethoxyphenyl- (**4**) and 2,2’-bithiophen-5-yl- (**5**) (Figure 1). The change of the substituents in the phenyl ring of IPh was realized to analyze the effect of substituent in ligand on the reduction. Thus, dimethylamino- (**2**) and dimethoxy- (**4**) substituents possess good donor characteristics. Ligand **3** is ditopic receptor able to coordinate Cu(II) cations through both the phenantroline and azadithticrown ether centers. The thiophene residue in **5** is suitable for stabilization of radicals arising upon the reduction process. The occurrence of reduction reaction was examined by optical, ESI-MS, electrochemical and quantum-chemical methods. Furthermore, we elucidated the factors governing this reduction reaction.



Scheme 1. Structures of ligands **1-5** applied for preparing of complexes with Cu(II).

Results and discussion

Ligands **1-5** complexes with $Cu(ClO_4)_2$ have been prepared and analyzed by optical, ESI-MS, elemental analysis, IR and electrochemical methods in MeCN. This solvent was chosen as more appropriate for stabilization of arising Cu(I) ions and because in this solvent the studied ligands as well as $Cu(ClO_4)_2$ have got sufficient solubility. Keeping of Cu(II) complexes in DMSO or ethanol showed that autoreduction process did not occur.

Complex formation study

UV–Vis electronic absorption spectra of IPh derivatives **1** - **5** in MeCN with concentration $2 \cdot 10^{-5}$ mol·L^{-1} at room temperature are shown in Fig.1. All the ligands display several strong absorption peaks with wavelengths shorter than 400 nm. The position of an intense long wavelength absorption band depends on the electronic nature of substituent R (Fig. 1). The presence of donor dimethoxy- (**4**) or especially dimethylamino-groups (**2, 3**) at position 4 of the aryl moiety results in the substantial red shift of long wavelength absorption band relative to that of ligand **1**. In case of ligand **5** functionalized with donor bithiophene substituent the largest shift of the long wavelength absorption band is observed because of more extended π-conjugation.

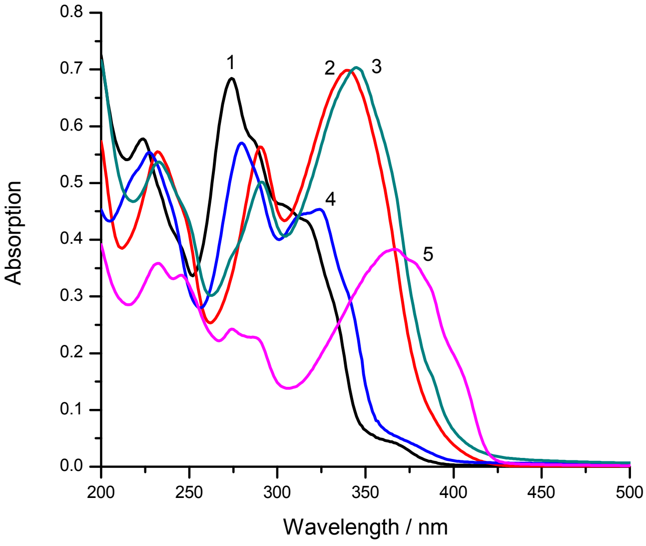


Figure 1. Electronic absorption spectra of IPh derivatives **1**(1), **2**(2), **3**(3), **4**(4), **5**(5) in MeCN, $C_{Lig} = 2 \cdot 10^{-5}$ mol·L^{-1}, T = 20°C.

The addition of Cu(II) perchlorate to a solution of **1** in MeCN resulted in a substantial changes in absorption spectrum, which are evidently due to formation of complexes of **1** with Cu^{2+} (Fig. 2). The strong distortion of an isosbestic points upon spectrophotometric titration of **1** with Cu^{2+} was observed, indicating more than one kind of complex formation.

To estimate the stoichiometry of prevailing ligand-metal complex the mole-ratio method and the method of continuous variations have been used (Figs. S15, S16 in SI). The analysis of spectrophotometric data (the mole-ratio method) showed the formation of complex $\mathbf{1}_3 \cdot Cu^{2+}$ as a major component at law metal to ligand ratio. The method

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of continuous variations indicates the formation of complexes $\mathbf{1}_3\cdot Cu^{2+}$ or $\mathbf{1}_2\cdot Cu^{2+}$.

The ESI-MS spectra were recorded for free ligands **1**-**5** and their copper complexes in the presence of 3-fold excess of ligand and 3-fold excess of $Cu(ClO_4)_2$ salt. The obtained spectra of complexes contain a set of peaks in which we found and analysed the peaks belonging copper complexes. To confirm the assignment of obtained peaks, the comparison of experimental and theoretical mass-spectra has been done (the examples of the comparison of theoretical and experimental mass-spectra are presented in Figs 3a and S1, S2 in SI).

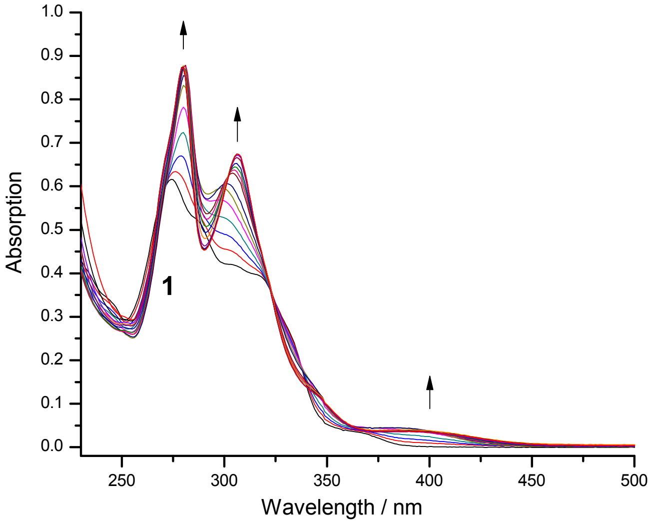

Figure 2. Electronic absorption spectra of **1** alone (1) and in the presence of increasing concentration of Cu^{2+}. Initial concentration of **1** was $C_1=1.8\times10^{-5}$ mol·L^{-1}, concentration of copper(II) perchlorate was varied from 0 to 0.00023 mol·L^{-1}. Solvent – acetonitrile, T = 294K.

According to ESI-MS analysis the formation of two types of complexes, namely, $\mathbf{1}_3\cdot Cu^{2+}$(m/z: $[476.5]^{2+}$) and $\mathbf{1}_2\cdot Cu^{2+}$(m/z: $[328]^{2+}$) has been observed depending on Cu^{2+} amount in solution (Scheme 2 and Figs. 3a, b and S2, S3 in SI). In the presence of 3-fold excess of ligand **1**, ESI-MS spectrum contains the peaks belonging to free ligand, complexes $\mathbf{1}_3\cdot Cu^{2}$ and $\mathbf{1}_2\cdot Cu^{2+}$ (Fig. 3a). At 3-fold excess of Cu^{2+} cations, the content of $\mathbf{1}_3\cdot Cu^{2+}$ decreases, the spectrum contains peaks of $\mathbf{1}_2\cdot Cu^{2+}$ with one perchlorate or one hydroxyl anion group (Fig. 3b). According to ESI-MS data the consequence formation of complexes $\mathbf{L}_3\cdot Cu^{2+}$ and $\mathbf{L}_2\cdot Cu^{2+}$ upon increase of Cu^{2+} amount is typical for all studied ligands **1**-**4** (see Figs. S4-S14 in SI).

Another important observation is that ESI-MS spectra of copper complexes of ligand **1** and **4** contain the complexes of Cu^{2+} ions only, whereas, in ESI-MS spectra of complexes of ligands **2** and **3** one can see remarkable amount of Cu^{+} complexes also especially at 3-fold excess of $Cu(ClO_4)_2$ salt. This fact is in good agreement with that the Cu(II)- Cu(I) autoreduction occurs in complexes with **2** and **3** ligands.

The ESI-MS analysis of Cu^{2+} complexes with **5** did not show the molecular peak due to intensive polymerization of ligand in curse of analysis. To avoid the polymerization of thiophene-containing ligands the mass-spectral analysis is usually carried out by using of soft ionization methods (MALDI, FAB)[39,40]. Unfortunately, these methods are not suitable for analysis of positively charged complexes.

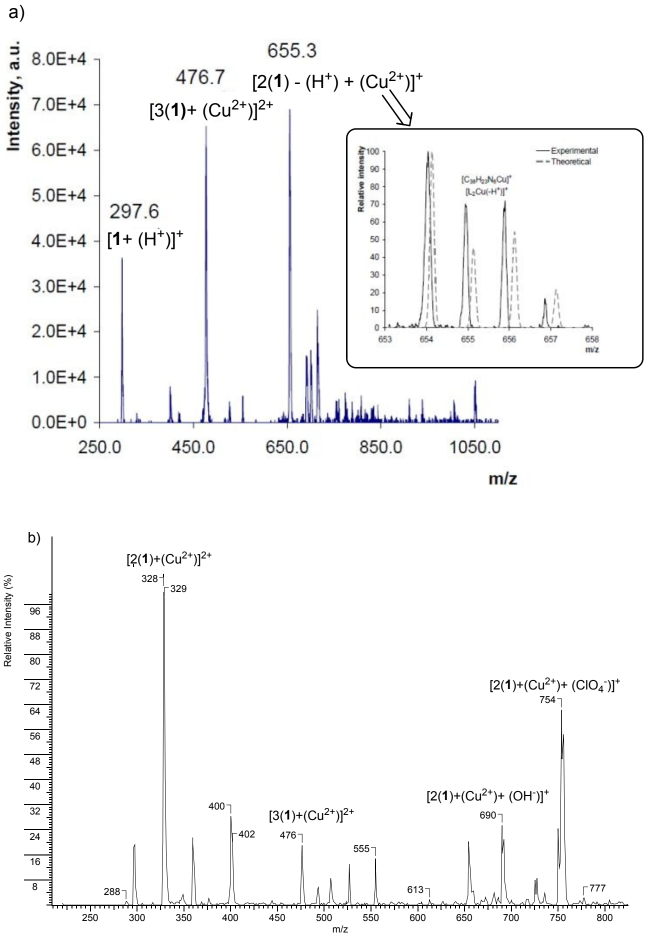

Figure 3. ESI-MS of a) mixture of ligand **1** with Cu^{2+}, ratio 3:1; b) ligand **1** in the presence of 3-fold excess of $Cu(ClO_4)_2$.

A series of copper(II) complexes with **1**-**5** in solid state were formed and precipitated out from acetonitrile solution when dry diethyl ether was added. At 3-fold excess of ligand $\mathbf{L_2}\cdot Cu^{2+}$ complexes were isolated and characterized by different physico-chemical methods (see Experimental part). According observation by elemental analysis, complexes with composition $\mathbf{L_3}\cdot Cu^{2+}$ can be isolated only in mixture with $\mathbf{L_2}\cdot Cu^{2+}$.

In accordance with the known literature data cited in the introduction of the paper, phenanthroline is the preferable place for Cu^{2+} ion coordination with imidazophenanthrolines. Nevertheless due to the complexity of the system we could

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not determine the stability constants for the complexes of **1** with Cu^{2+} by direct spectrophotometric titration method.

Density functional theory (DFT) and its extension to time dependent density functional theory (TD-DFT) were performed to study the molecular structure, electronic and spectroscopic properties of copper with the4-dimethylaminophenyl ligand **2**. The ligand **2** possesses two site of complexation though the phenantroline (Phen) or imidazole (Im) units and can coordinate the copper as a bidentate or mono-dentate manner *via* the pyridine nitrogen or imidazole nitrogen atoms. To determine the most favorable site of coordination for **2** with copper we optimized the geometries and calculated the binding energies for Cu^{2+} and Cu^{+} complexes involving several numbers of ligands. Indeed since the ligand can coordinate as bidentate or mono-dentate and to ensure a tetrahedral or square-planar environment about copper we studied complexes involving two, three and four ligands. The Figs 4 and S28, S29 in SI show the calculated geometries of complexes $\mathbf{2}_2\cdot Cu^{2}$ (Phen$_2$), $\mathbf{2}_3\cdot Cu^{2+}$(PhenIm$_2$), $\mathbf{2}_4\cdot Cu^{2+}$(Im$_4$), $\mathbf{2}_2\cdot Cu^{+}$(Phen$_2$), Cu^{+}(PhenIm$_2$) and $\mathbf{2}_4\cdot Cu^{2+}$(Im$_4$). In title of complexes type (Phen – phenantroline and Im – imidazole) and quantity of binding sites are presented in parentheses.

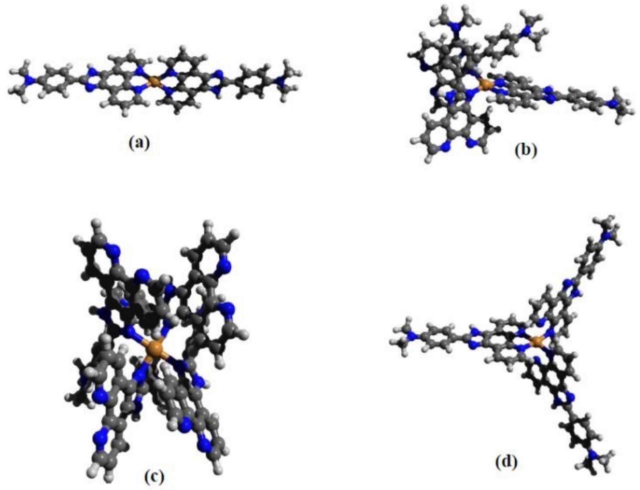

Figure 4. The optimized structure of (a) $\mathbf{2}_2\cdot Cu^{2+}$(Phen$_2$) (coordination of metal ion with two phenantroline moieties); (b) $\mathbf{2}_3\cdot Cu^{2+}$(PhenIm$_2$) (coordination of metal ion with one phenantroline and two imidazole moieties); (c) $\mathbf{2}_4\cdot Cu^{2+}$(Im$_4$) (coordination of metal ion with four imidazole moieties); and (d) $\mathbf{2}_3\cdot Cu^{2+}$(Phen$_3$) (coordination of metal ion with three phenantroline moieties).

From energetic point of view we calculated the binding energy defined as follows:

$$\Delta E = E_{complex} - E_{Copper} - \sum_i E_{ligands}$$

(*i*=2, 3 or 4 depending the complex).

The energies binding gathered in Table 1 clearly show that complexation of the phenantroline site is most favorable than the imidazole site whatever the charge of the complex. The binding energy decreases in the order $\mathbf{2}_2\cdot Cu^{2+}$(Phen$_2$) > $\mathbf{2}_3\cdot Cu^{2+}$(PhenIm$_2$) > $\mathbf{2}_4\cdot Cu^{2+}$(Im$_4$) demonstrating that the complexation through the imidazole leads to a less strong bond than with phenantroline moiety. Similar trend is found with Cu^{+} complexes.

Table S1 in SI lists some main geometrical characteristic of the calculated complexes. The dihedral angle between the planes defined by the copper centre and each set of nitrogen atoms is found to be 80.8° and 81.2° in the $\mathbf{2}_2\cdot Cu^{2+}$(Phen$_2$) $\mathbf{2}_2\cdot Cu^{+}$(Phen$_2$) complexes. These angles are slightly smaller than the 90° value expected for regular tetrahedral geometry.

Table 1. Binding energies (in kcal/mol) in the copper (Cu^{2+} or Cu^{+}) complexes with ligand **2** through imidazole (Im) or phenantroline (Phen) units.

	ΔE
$\mathbf{2}_3\cdot Cu^{2+}$(Phen$_3$)	-207.4
$\mathbf{2}_3\cdot Cu^{+}$(2-Phen$_3$)	-77.0
$\mathbf{2}_2\cdot Cu^{2+}$(Phen$_2$)	-185.9
$\mathbf{2}_3\cdot Cu^{2+}$(PhenIm$_2$)	-173.8
$\mathbf{2}_4\cdot Cu^{2+}$(Im$_4$)	-129.1
$\mathbf{2}_2\cdot Cu^{+}$(Phen$_2$)	-82.2
$\mathbf{2}_3\cdot Cu^{+}$(PhenIm$_2$)	-65.7
$\mathbf{2}_4\cdot Cu^{+}$(Im$_4$)	-47.5

This change from tetrahedral to planar square when the number of imidazole interacting with copper increases seems to be correlated with the increase of the Cu…N distances. In the mixed complex involving both phenantroline and imidazole, the geometry of the nitrogen atoms around the copper is found strongly distorted and in between tetrahedral and square-planar.

Therefore it is clear from calculations that the phenanthroline moieties impose a tetrahedral mode of complexation while the coordination through imidazole unit leads to a more square planar arrangement.

Autoreduction of Cu(II) to Cu(I) in complexes with IPh ligands

It should be pointed out that the solution of Cu^{2+} complexes with ligand **1** remains stable over time at any excess of copper cations, so that the changes in absorption spectrum were not observed even after a few days. Another behavior was observed for ligands **2**, **3**. The addition of Cu(II) perchlorate to a solution of **2** in MeCN in molar ratio 1:3 resulted in a small red shift of long wavelength absorption band due to complex formation (Fig. 5).

However at molar ratio 10:1 the new intensive absorption band at 766 nm appears immediately after Cu^{2+} addition. The spectrum recorded at molar ratio 10:1 demonstrates significant changes in time, consisting in the fact that the intensity of the 766 nm band decreases and

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simultaneously a new band at 463 nm is appeared (Fig. S17 in SI). The observed band at 766 nm could be assigned as LMCT band. The LMCT excited state arises as a result of promotion of an electron from ligand-localized fully occupied orbitals to a not completely filled 3d-orbital of a copper ion. The LMCT excited states of Cu(II) complexes have been thoroughly reviewed in the literature.[30] Therefore, ligand **2** → Cu(II) LMCT is expected to result in reduction of Cu(II) with the formation of copper(I) complex. In our case, the autoreduction of Cu(II) to Cu(I) complexes occurs spontaneously in the dark and without additional reducing agents in about 80 min. As a result, after 80 minutes the intensity of the band at 766 nm disappears, and the intensity of the 463 nm band reaches its maximum value (Fig. S18 in SI). The absorption band at 463 nm could be assigned to MLCT transition in Cu(I) complex.[19] The absorption bands centered at 292 and 336 nm which could be assigned to intraligand π→ π* transitions[31] also changed their positions and intensity.

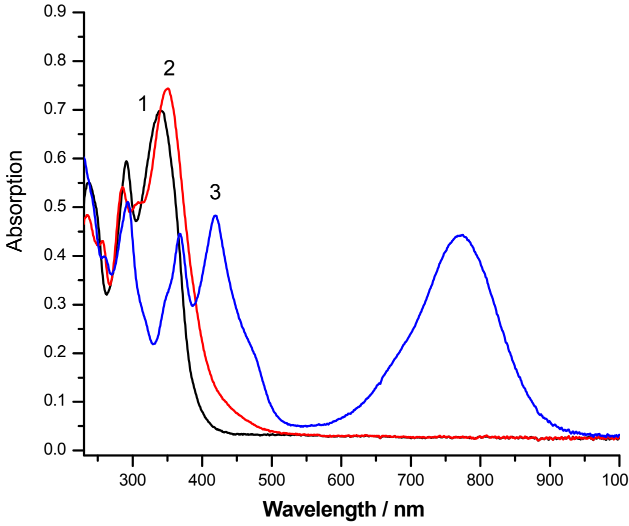
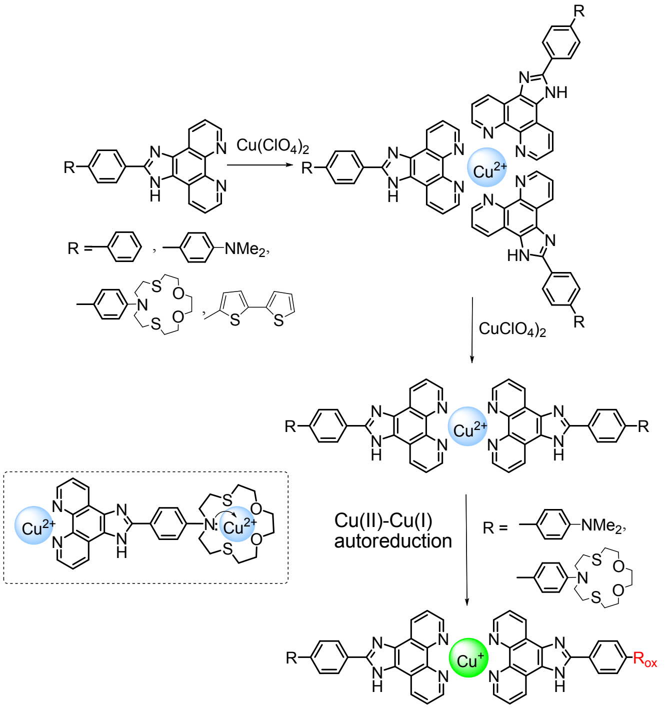


Figure 5. Electronic absorption spectra of $2{\times}10^{-5}$ mol·L^{-1} of **2** alone (1) and in the presence of $6.67{\times}10^{-6}$ mol·L^{-1} (2) and $1{\times}10^{-4}$ mol·L^{-1} (3) $Cu(ClO_4)_2$. Spectra (2) and (3) were recorded in 10 sec after $Cu(ClO_4)_2$ addition. Solvent – acetonitrile, T = 294K.

The observed autoreduction of Cu(II) to Cu(I) is provided by at least three reasons. These are the presence of donor substituent in the phenyl ring of ligand **2**, the geometry around the copper ion and the solvent effect. While the strong donor N,N-dimethylaniline in ligand **2** provides the occurrence of LMCT, ligand **1**, lacking N,N-dimethylamino group, did not show the LMCT transition and autoreduction of Cu(II). At large excess of ligand **2** the complex $\mathbf{2}_3{\cdot}Cu^{2+}$ was formed. For trisbidentate chelates of Cu(II), like the complex $\mathbf{2}_3{\cdot}Cu^{2+}$, the stable tetragonally distorted octahedral configuration about Cu(II) could be expected.[32] The addition of copper(II) cations to complex $\mathbf{2}_3{\cdot}Cu^{2+}$ should lead to the formation of $\mathbf{2}_2{\cdot}Cu^{2+}$ complex similar to what was observed for ligand **1**. The results of ESI-MS observation supported interpretation and are presented in Figs. S6 in SI. The formation of $\mathbf{2}_2{\cdot}Cu^{2+}$ complex is believed to force a tetrahedral geometry about the copper atom and induces a positive shift in the reduction potential providing the occurrence of autoreduction of Cu(II).[19] The effect that Cu^{2+} to Cu^{+} transformation occurs more effectively in the presence of excess of $Cu(ClO_4)_2$ salt was firstly observed and described in detail for dioximate complexes of Cu^{2+}.[31] Finally, the stabilization of Cu(I) in MeCN solution was described earlier in literature.[31,33]



Scheme 2. Complex formation of ligands **1-5** with Cu^{2+} cations and Cu(II)-Cu(I) autoreduction.

Ligand **3** contains macrocyclic azadithiacrown ether moiety. Cu^{2+} can form complexes with **3** through coordination via both macrocyclic and heterocyclic parts of the molecule (Scheme 2).[34] The formation of complex $\mathbf{3}_3{\cdot}Cu^{2+}$ causes the shift of absorption bands presented in Fig. 6. The presence of excess of Cu^{2+} cations leads to the appearance of additional intensive band centered at 836 nm which could be assigned as LMCT band in Cu(II)-ligand **3** complex in view of its high molar extinction coefficient (ε = 12000 L mol^{-1} cm^{-1}) (Fig. 6). The conformation of the macrocyclic-Cu(II) complex may affect the position of the LMCT band at 836nm in Cu(II)-ligand **3** complex which is bathochromically shifted relative to these for ligand **2** (766 nm). Also some complexes of Cu(II) with azadithiacrown ether demonstrated the long wavelength band in region near 800 nm.[35,36]

The changes in UV-Vis spectra of ligand **3** in the presence of 10-fold excess of $Cu(ClO_4)_2$ during 40 minutes at ambient temperature are shown in Fig.S18 in SI. Copper(II) seems to be reduced partly by a concomitant oxidation of coordinated ligands. According ESI-MS spectra (Fig. S10 in SI) the formation of mixed-valence Cu(I)/Cu(II) complex of **3** was observed. Earlier it was found that in binuclear dicopper(II) ligand based on benzoimidazole the autoreduction occurs and the mixed-valence Cu(I)/Cu(II) complex is more stable in comparison with Cu(II)/Cu(II) one.[21]

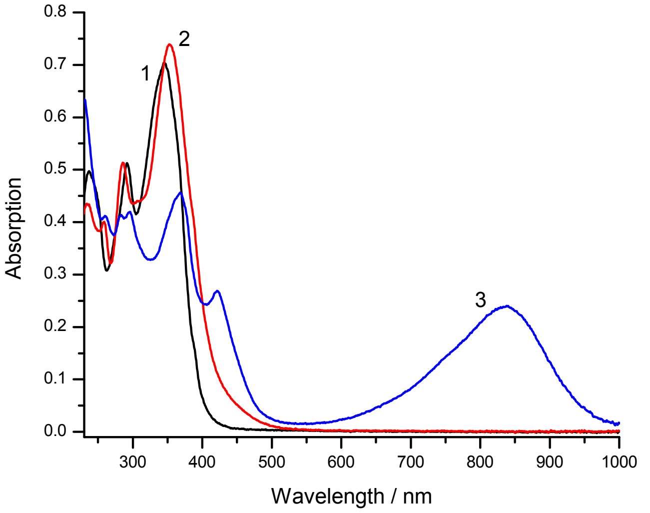
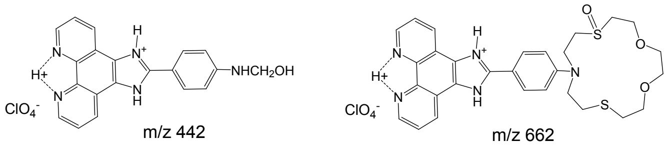


Figure 6. Electronic absorption spectra of 2×10^{-5} mol·L^{-1} of **3** alone (1) and in the presence of 6.67×10^{-6} mol·L^{-1} (2) and 1×10^{-4} mol·L^{-1} (3) $Cu(ClO_4)_2$. Spectra (2) and (3) were recorded in 10 sec after $Cu(ClO_4)_2$ addition. Solvent – acetonitrile, T = 294K.

From ESI-MS spectra (Figs. S7 and S11 in SI) recorded after keeping of complexes $\mathbf{2}_2{\cdot}Cu^{2+}$ and $\mathbf{3}_2{\cdot}Cu^{2+}$ for 48 hours we proposed the structure of oxidized ligands (Scheme 3). The obtained peak with m/z 442 belongs to phenylimidazophenetroline ligand with hydroxymethylamino substituent at 4-th position in phenyl ring. Thus, NMe_2 group is involved in oxidation process. In ligand **3** the oxidation occurs with participation of sulphur atom of macrocyclic residue as showed in Scheme 3 below.



Scheme 3. The proposed structure of oxadized ligands **2** and **3**.

The ligands **4** and **5** display strong absorption bands at short wavelength (200-400nm) that can be assigned as intraligand π– π* transitions. Addition of $Cu(ClO_4)_2$ to ligands **4** and **5**, even in a large excess, has a much smaller effect on the absorption spectra as compared with ligands **2** and **3**, so that the appearance of an intensive long-wave absorption band in the 650-950 nm region was not observed (Figs.S19-S22). The low-intensive absorption in the range of 420-480 nm in copper(II) complexes of ligand **4** could be assigned as LMCT based on the earlier obtained results on copper(II) complexes with bipyridine ligand.[37] The absorption in this region slightly increases for 40 minutes, which was not observed in the case of ligand **1** (Fig. S17 in SI).

The calculated absorption spectrum of **2** (Figure 7 and Figure S30 for a more detailed description) is found in good agreement with the experimental and indicate a large absorption around 350 nm arising from two single excitation at 369 nm (*f*=0.359) and 331 (*f*=0.915). These absorptions can explain the strong absorption peak around 350 nm. It could be noted that a weak electronic transition is calculated at 404 nm and is assigned to a charge transfer excitation from the amino-phenyl to the phenantroline part of the ligand.

TD-DFT calculations in acetonitrile were performed with the B3LYP, M062X and MPW1PW91 functionals on the most stable complexes $\mathbf{2}_2{\cdot}Cu^{2+}$ and $\mathbf{2}_2{\cdot}Cu^{+}$. The spin-allowed predicted transitions (singlet–singlet for ligand **2** and $\mathbf{2}_2{\cdot}Cu^{+}$ complex and doublet–doublet for $\mathbf{2}_2{\cdot}Cu^{2+}$ complexes) are listed in Table 2 and Table S2 in SI as well as with their assignment. Comparison of TDDFT results with experimental data reveals that B3LYP functional produce optical spectrum which is more close to experiment and only these results will discuss in the following.

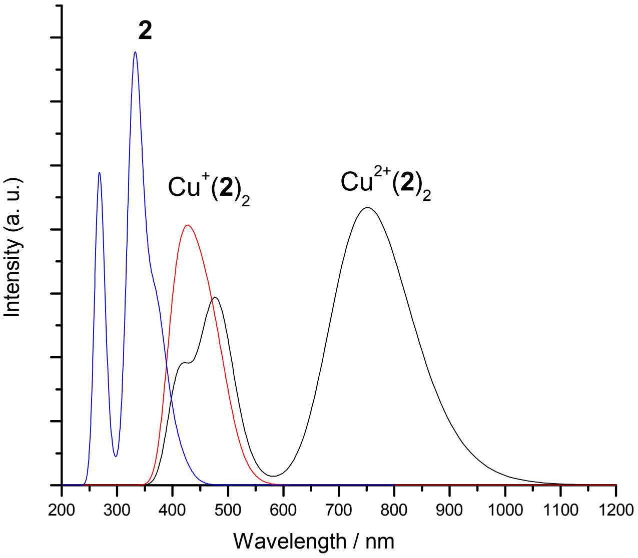


Figure 7. B3LYP calculated absorption spectra of ligand **2** (blue) and the complexes $Cu^{2+}(\mathbf{2})_2$ (black) and $Cu^{+}(\mathbf{2})_2$ (red).

For the $\mathbf{2}_2{\cdot}Cu^{2+}$ complex the calculations predicted a strong allowed transition at 751 nm, at the B3LYP level of calculation. The orbitals implied in the transition are displayed in Figure S33 in SI and show that H-8(β) corresponds to π orbital delocalized on the ligand **2** while the LUMO(β) is π* orbital mainly on the phenantroline moiety on the same ligand. Therefore this transition can be characterized as ligand charge transfer transition (LCT). The

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analysis of the electron population in the complex shows a significant charge transfer from ligand to copper in the ground state of complex. Indeed the calculated Mulliken charge on copper is found to be +0.28. Therefore, the remain charge (+1.72) of the complex is distributed on the ligand suggesting that their optical properties could be different from the neutral state. To test this hypothesis, we calculated the optical properties of cationic state of the ligand **2** and compared the obtained results with that of neutral state (see supporting information Figs. S30, S31 in SI). The result clearly shows a large bathochromic shift of the maximum absorption upon oxidation of the ligand. This simple calculation suggests that the absorption at 751 nm of the $\mathbf{2}_2{\cdot}Cu^+$ is the result of the ligand charge transfer in the complex. The appearance of strong absorption around 750 nm is strongly related to the nature of the ligand. We calculated the optical properties of the copper complex with the ligand **1** and the obtained absorption spectrum showed no significant absorption in infrared region in agreement with experiment observation (see supporting information Figure S32).

Table 2. Selected computed UV-vis energies transitions in acetonitrile for $\mathbf{2}_2{\cdot}Cu^{2+}$ and $\mathbf{2}_2{\cdot}Cu^+$ complexes calculated at the B3LYP level.

States	λ_{calc} (nm)	Oscillator strength (*f*)	Assignment[a]	Character[b]
$\mathbf{2}_2{\cdot}Cu^{2+}$ (Phen$_2$)				
S_8	751	0.599	H-8(β)→L(β)	LCT
S_{21}	479	0.221	H-1(α)→L(α), H(α)→L+2(α), H-2(β)→L+2(β)	MLCT + $\pi \rightarrow \pi^*$
S_{22}	479	0.134	H2(α)→L+2(α), H(α)→L+4(α), H(β)→L+2(β)	MLCT
S_{26}	465	0.028	H-1(α)→L(α), H(α)→L+2(α), H-1(β)→L+1(β)	$\pi \rightarrow \pi^*$
$\mathbf{2}_2{\cdot}Cu^+$ (Phen$_2$)				
S_2	475	0.252	H-1→L+1, HOMO→LUMO	$\pi \rightarrow \pi^*$
S_7	436	0.325	H-3→LUMO, H-2→L+1	MLCT
S_8	406	0.309	H-1→L+2, HOMO→L+3	$\pi \rightarrow \pi^*$

[a] H=HOMO, L=LUMO. [b] MLCT = ligand to metal charge transfer, LCT = ligand charge transfer

After reduction of the copper in the $\mathbf{2}_2{\cdot}Cu^+$ complex, the calculated spectra show three allowed electronic transitions at 475, 436 and 406 nm. The first lowest transition originate from H-1→L+1, HOMO→LUMO single excitations. HOMO and H-1 are similar and localized on the amino-phenyl part of the ligand while both LUMO and LUMO+1 are mainly distributed on the part of the ligand in close interaction with the copper. This electronic transition is then a $\pi \rightarrow \pi^*$ charge transfer on the ligand. The second transition is built on single excitations involving H-2 or H-3 localized on copper to LUMO or LUMO+1 localized on phenantroline part of the ligand. This transition can thus be characterized as a metal to ligand charge transfer (MLCT) transition. The electronic transition calculated at 406 nm is a charge transfer electronic transition localized on the ligand as previously showed.

Voltammetry studies

To determine the redox potentials of complexes, cyclic voltammograms of all the ligands and their Cu(II) complexes were recorded in MeCN solvent using *tetra*-butylammonium perchlorate (TBAP) as a supporting electrolyte. Cyclic voltammograms of $Cu(ClO_4)_2$, ligands **1**-**5** and their complexes with copper(II) are shown in Figs. S23-S24 in SI. The obtained values of E_p^{Red} and E_p^{Ox} are collected in Table 3. The cyclic voltammetry curve of $Cu(ClO_4)_2$ (Fig. S23 in SI, Table 4) show two couples at the following peak potentials: 1.04/1.13 and -0.67/-0.44. The first reversible step corresponded to Cu(II) →Cu(I) transformation, the second pair describes Cu(I)→Cu(0) reduction. Also after the second step of the reduction process the desorption of metallic copper on electrode was observed.

Table 3. Electrochemical data in MeCN with 0.1 M TBAP as supporting electrolyte; potentials were measured relative to Ag|AgCl|KCl aq. sat. reference electrode. The potentials of the peaks on the reverse scans of the cyclic voltammetry curves are given after the slash.

Compound	E_p^{Red}, V	E_p^{Ox}, V (ΔE_p^{Ox}, mV)
$Cu(ClO_4)_2$	1.04/1.13; -0.67/-0.44;-0.19*	-
1	-	1.13; 1.45; 1.65
1:Cu^{2+} (1:3)	0.47; 0.20; -0.61;	1.55 (420); 1.69
2	-	0.75; 1.01; 1.62;1.81
2:Cu^{2+} (1:3)	0.83/1.00; 0.47; 0.20; -0.69	1.31 (560); 1.56; 1.75
3	-	0.97; 1.36; 1.52
3:Cu^{2+} (1:1)	0.51; 0.30; -0.78	1.32; 1.55

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3:Cu^{2+} (1:3)	0.42; 0.20; -0.76	1.28 (310); 1.60
4	-	1.08; 1.42; 1.66
4:Cu^{2+} (1:3)	0.54; 0.22; -0.64;	1.43 (350)
5	-	1.42
5:Cu^{2+} (1:3)	0.64; -0.39	1.66 (240)

*

oxidative desorption of copper(0) on electrode

In the presence of Cu^{2+} cations the first oxidation peak of ligands **1**-**5** was found to be anode shifted up to ΔE_p^{Ox} = 240-560 mV suggesting the occurring of complex formation with all studied ligands (Table 2). Furthermore, in complexes Cu(II)→Cu(I) and Cu(I)→Cu(0) reduction exhibits peaks differ than those for free Cu(II) perchlorate. The complexation is corroborated by an appearance of the additional peaks corresponding to the Cu(II)→Cu(I) and Cu(I)→Cu(0) reduction processes at the potentials differing from that one of free Cu(II) perchlorate.

From one point of view, the tendency of the oxidation and reduction potential changes upon complex formation with Cu(II) of all studied ligands are similar what can be explained by the formation of one type of complexes when copper cation is coordinated with phenantroline part of each ligands. Also the found changes are similar to what was early observed for described in literature aryl-1H-imidazole[4,5f][1,10]phenanthroline Cu(II) complexes.[15] Otherwise, the electrochemical behavior of each ligands in the presence of copper cations has got some peculiarities. Thus, the oxidation of **2** proceeds *via* several one electron steps; with the initial two steps presumably involving the amino group (Fig. 8, Table 3). The addition of 3-fold excess of copper(II) perchlorate causes a color change of the solution that turns to purple and then to colorless. The reduction cyclic voltammetry curves of the complexes were recorded at potential between 1.3 V and –1.0 V (i. e. in the reduction of Cu(II) region) each hour for 4 hours until the cyclic voltammograms became unchanged (Fig. 8). The obtained cyclic voltammograms demonstrated the series of E_p^{Red} peaks belonging to reduction of the copper(II). The reduction peak of Cu(II)→Cu(I) from Cu(II) perchlorate taken in the excess along with the two reduction peaks of Cu(II)→Cu(I) at 0.47 V and 0.20 V from the complexed Cu(II) are present at positive potentials. The remarkable increase of Cu(I)→Cu(0) reduction peak at E_{pc} = -0.69 V was also observed. This phenomenon could be connected with occurring of autoreduction process producing increasing amount of Cu(I).

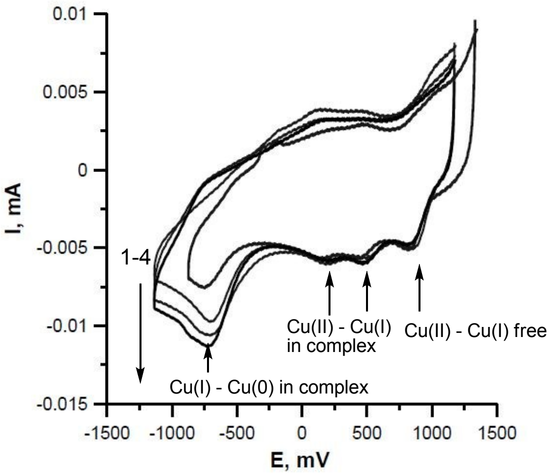

Figure 8. Changes in cyclic voltammogram of 1.67·10^{-4}M solution of ligand **2** in the presence of 3-fold excess of copper(II) perchlorate (1-4) recorded each one hour during 4 hours in 0.1 M TBAP in MeCN at 200 mV/s.

From the obtained data we can propose that the reduction of Cu(II) in complex with ligand **2** proceeds through the electron transfer from dimethylamino group of **2**. Indeed, there are no oxidation peaks associated with the dimethylamino group in the cyclic voltammogram of the complex (Fig. 9). This fact is in agreement with ESI-MS data pointed on the occurring of oxidation of NMe_2 group after keeping of $\mathbf{2}_2$·Cu2$^+$ complexes for some hours. The important condition for successful ligand-copper(II) electron transfer process is overlapping of the oxidation potential of ligand **2** ($E_{1/2}$ 0.75 V) with the reduction potential of the Cu^{2+}/Cu^+ ($E_{1/2}$ 1.085 V).

The electrochemical behavior of ligand **3** depends on the amount of copper(II) presented in the acetonitrile solution (Fig. 9).

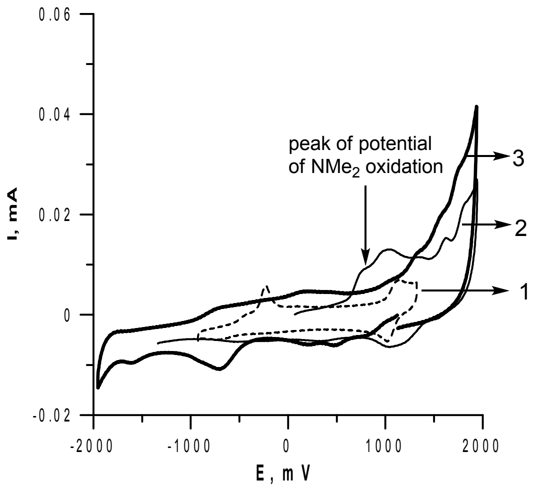

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Figure 9. Cyclic voltammogram of 1.67·10^{-4}M solution of Cu(ClO_4)$_2$ (1), ligand **2** (2) and complex of **2** formed in the presence of 3-fold excess of copper(II) (3) recorded after keeping for 4 hours in 0.1 M TBAP in MeCN at 100 mV/s.

As with ligand **2**, the oxidative potential of ligand **3** (0.97 V) overlaps the reduction potential of Cu(II), although to the less extend. Thus, when ratio **3**:Cu^{2+} is 1:1, the remarkable increase of Cu(I)→Cu(0) reduction peak at E$_{pc}$ = -0.75 V was observed similar to that we have observed for ligand **2** (Table 3, Fig. 10). This phenomenon is explained by occurring of autoreduction process producing increasing amount of Cu(I). Because the phenantroline moiety is the preferable site for binding of copper(II), all cations are bound with this part of ligand. Thus, the uncomplexed crown ether moiety acts as a donor group in the Cu(II) reduction process. In the presence of 3-fold or more excess of copper(II) the Cu(I)→Cu(0) reduction in complex with **3** is not observed. This is because the copper(II) at this condition is coordinated both with IPh and with azathiacrown ether part switching the donor macrocycle from the conjugation with IPh chromophore (Fig. S24 in SI). The ESI-MS analysis supports the formation of complexes through the macrocycle part at the excess of copper(II) (Fig. S10 in SI). The interpretation of electrochemical data obtained in this study has been done by taking into account the results of electrochemical observation of Cu(II) complex with thia-containing ligands[52] and Cu(II)→Cu(I) autoreduction in complex with some ligands cited in the Introduction.[16-20]

The Cu(II) → Cu(I) autoreduction process for the complexes of ligands **1**, **4** has not been observed (Fig. S25, S26 in SI). This is obviously due to the oxidation potentials of ligands **1**, **4** do not overlap with the reduction potential of Cu(II) → Cu(I). Our attempts to study the complex formation of ligand **5** failed due to its poor solubility in acetonitrile and polymerization on the electrode (Fig. S27 in SI).

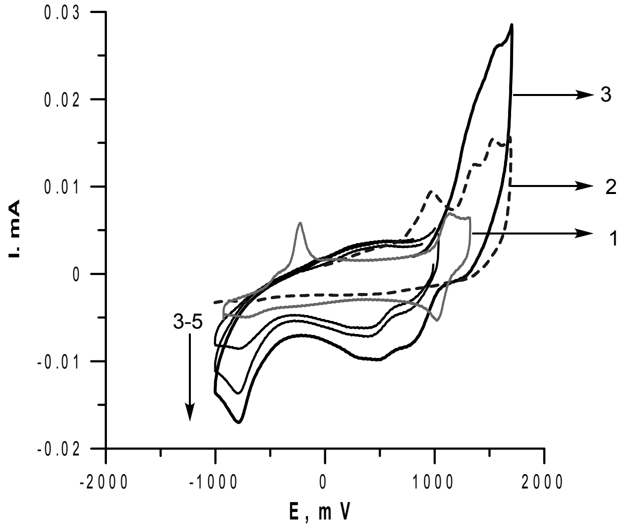


Figure 10. Cyclic voltammogram of 1.67·10^{-4}M solution of Cu(ClO_4)$_2$ (1), ligand **3** (2) and in the presence of copper(II) (3-5) (ratio 1:1) recorded each one hour during 4 hours in 0.1 M TBAP in MeCN at 100 mV/s.

Experimental

Materials

Phenantoline-5,6-dion, benzaldehyde, 4-(dimethylamino)benzaldehyde, 3,4-dimethoxybenzaldehyde, 2,2'-bithiophene-5-carbaldehyde, ferrocene, Cu(ClO_4)$_2$·6H_2O, tetrabutylammonium perchlorate (TBAP) (Fluka) were commercially available and were used without further purification. 4-(1,4-Dioxa-7,13-dithia-10-azacyclopentadecan-10-yl)benzaldehyde was prepared as described elsewhere.[31] Anhydrous acetonitrile (MeCN) and dimethylformamide (DMF) for electrochemical measurements were electronic grade purity and were used as received. Spectroscopic grade MeCN was used for recording of the absorption spectra**.**

Instruments

^{1}H NMR and ^{13}C (APT-method) spectra were recorded on a Bruker Avance 400 (operating frequency 400.13 MHz, 100.61 MHz) and Avance 600 (operating frequency 600.22 MHz, 150.93 MHz) spectrometers using DMSO-d$_6$ as a solvent and the internal standard. The chemical shifts and spin-spin coupling constants were determined with accuracy of 0.01 ppm and 0.1 Hz, respectively.

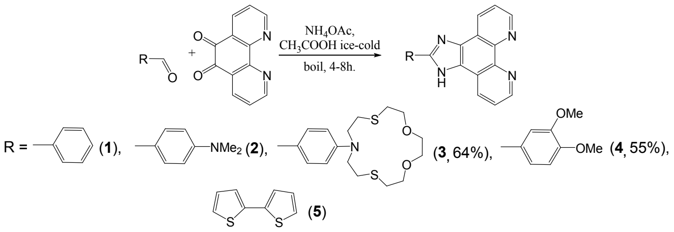
ESI mass spectra (ESI-MS) were acquired on a Finnigan LCQ Advantage tandem dynamic mass spectrometer (USA) equipped with a mass analyzer with an octapole ionic trap, a MS Surveyor pump, a Surveyor autosampler, a Schmidlin-Lab nitrogen generator (Germany), and a system of data collection and processing using the X Calibur program, version 1.3 (Finnigan). The mass spectra were measured in the positive ion mode. Samples in MeCN were injected directly into the source at flow rate 50 µL min^{-1} through a Reodyne injector with a loop of 20 µL. The temperature of the transfer capillary was 150°C, and the electrospray needle was held at potential 4.0 kV.

UV-Vis spectra were measured using two channel spectrophotometer Varian-Cary 300, and Avantes AvaSpec-2048 spectrophotometer.

Electrochemical measurements were carried out at 22°C with an IPC-Pro M potentiostat. Cyclic voltammetry experiments were performed in a 1.0 mL cell equipped with a glassy carbon (GC) electrode (disk d=2 mm), Ag/AgCl/KCl (aq. saturated; reference electrode), and platinum electrode (counter electrode). The complexes were dissolved in degassed dry CH_3CN or DMF containing TBAP as the supporting electrolyte (0.10 M). Dry argon gas was bubbled through the solutions for 30 min before cyclic voltammetry experiments. The scan rate was 200 mVs^{-1}. A 1 mM solution of ferrocene along with 0.1 M TBAP in the respective solvents were employed during calibration. The number of electrons transferred was determined by comparing with the height of Fc^{2+}/Fc^{3+} wave for the same concentration and by rotating disk electrode method (RDE) as well. The same cell and electrodes were used for measurements carried out by RDE method. The rate of rotating was 2800 min^{-1}. The solutions of $Cu(ClO_4)_2{\cdot}6H_2O$ with concentration $5{\cdot}10^{-4}$ M, and ligands with $C_{ligand} = 1.67{\cdot}10^{-4}$ M were used.

Synthesis of ligands

Synthesis of 2-phenyl-1H-imidazo[4,5-f][1,10]phenantrolines 1-5 were carried out as described in [38]. The synthetic procedure includes the reaction of phenatroline-5,6-dione with corresponding aldehyde at reflux in the presence of ammonium acetate in a solution of glacial acetic acid for 4-8 hours (Scheme 4). The physicochemical characteristics of the compounds **1**, **2**, **5** are described in[39-41]. The structures of novel compounds **3**, **4** were confirmed by ^1H, ^{13}C NMR spectroscopy, elemental analysis and mass-spectrometry methods (Figs. S8, S12 in SI).



Scheme 4. Synthetic scheme of compounds **1**-**5** preparing.

2-[4-(1,4-Dioxa-7,13-dithia-10-azacyclopentadecan-10-yl)phenyl]-1H-imidazo[4,5-f][1,10]phenanthroline (3). 4-(1,4-dioxa-7,13-dithia-10-azacyclopentadecan-10-yl)benzaldehyde (0.338 mmol, 120 mg), 1,10-phenanthroline-5,6-dione (0.338 mmol, 71 mg) and ammonium acetate (6.6 mmol, 520 mg) were dissolved in 5 ml of glacial acetic acid. The mixture was stirred for 7 hours at reflux. An aqueous solution of NH_4OH (13%) was added to pH ~ 8. The precipitate formed was filtered on a glass porous filter, washed with water and diethyl ether. After washing the sediment was boiled in 10 ml of ethyl alcohol for 10 minutes, filtered and dried on a rotary evaporator at 75° C. The pure product was obtained as a beige precipitate (118 mg, 0.216 mmol). Yield 64%. ^1H NMR (DMSO-d$_6$, δ; ppm, J/Hz): 2.74 (t, 4H, ^3J=5.5), 2.84 (t, 4H, ^3J=7.2) [CH_2S], 3.56 (m, 4H, CH_2N), 3.68 (m, 8H, CH_2O), 6.80 (d, 2H, ^3J=8.8, Ph), 7.79 (m, 2H, IPh), 8.06 (d, 2H, ^3J=8.8, Ph), 8.87 (m, 2H, IPh), 8.98 (m, 2H, IPh), 13.37 (s, 1H, NH). ^{13}C NMR (DMSO-d$_6$, δ; ppm, J/Hz): 29.06, 30.69 (2CH_2S), 51.19 (2CH_2N), 70.00, 72.89 (2CH_2O), 111.49 (2CH), 117.39 (2C), 119.25 (C), 122.99, 123.22 (CH), 123.65, 125.78 (C), 127.77 (2CH), 129.32, 129.53 (CH), 135.72, 143.06, 143.45 (C), 147.27, 147.50 (CH), 147.83, 151.58 (2C). ESI-MS 3 in MeCN, *m/z*: calcd. 357.17; found 357.18 $[3+H]^+$. Calculated for $C_{29}H_{31}N_5O_2S_2$ (%): C, 63.83; H, 5.73; N, 12.83, found (%): C, 63.51; H, 5.78; N, 12.72.

2-(3,4-Dimethoxyphenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (4). By using of a similar technique a mixture of 3,4-dimethoxybenzaldehyde (0.476 mmol, 80 mg), 1,10-phenanthroline-5,6-dione (0.476 mmol, 100 mg) and ammonium acetate (9.5 mmol, 730 mg) was refluxed in 7 ml of glacial acetic acid for 7 hours. The precipitate formed was filtered on a glass porous filter, washed with water and diethyl ether and dried on a rotary evaporator at 75°C. The pure product was obtained as a beige powder (93 mg, 0.261 mmol). Yield 55%. ^1H NMR (DMSO-d$_6$, δ; ppm, J/Hz): 3.83 (s, 3H), 3.91 (s, 3H) [OCH_3], 7.16 (d, 1H, ^3J=8.8, Ph), 7.80 (m, 2H, IPh), 7.85 (d, 1H, ^3J=8.8, Ph), 7.86 (s, 1H, Ph), 8.91 (m, 2H, IPh), 8.99 (m, 2H, IPh). ^{13}C NMR (DMSO-d$_6$, δ; ppm, J/Hz): 55.62, 55.68, 109.73 (C), 111.87(C), 119.22(C), 121.59 (CH), 122.91 (2CH), 123.15 (2C), 123.18 (C), 129.63 (2C), 143.40 (2CH), 147.53(2C), 148.95(CH), 150.08 (CH), 151.02 (CH), 172.82 (CH). ESI-MS 4 in MeCN, *m/z*: calcd. 546.13; found 546.14 $[4+H]^+$.Calculated for $C_{21}H_{16}N_4O_2$ (%):C, 70.77; H, 4.53; N, 15.72, found (%): C, 70.66; H, 4.61; N, 17.58.

Synthesis of complexes

The solutions of complexes of ligands **1**-**5** with Cu(II) were prepared by the addition of required amount of $1{\cdot}10^{-1}$ M $Cu(ClO_4)_2{\cdot}6H_2O$ to $1.67{\cdot}10^{-5}$ M (for UV-Vis spectroscopy) or $1.67{\cdot}10^{-4}$ M (for electrochemical measurements) solutions of ligand in MeCN in order to obtain a ligand-copper ratio from 3:1 to 1:10. The analysis of complexes was made by UV-Vis spectrophotometry and ESI-MS spectrometry. The UV-Vis spectra were recorded for 100 minutes at intervals of 10 seconds.

The copper(II) complexes in solid state were synthesized following a common procedure as described below, using copper(II) perchlorate hexahydrate and the respective organic ligands.

Cu(**1**)$_2(H_2O)](ClO_4)_2$. To a suspension of **1** (26.5 mg, 0.09 mmol) in 25 mL acetonitrile, $Cu(ClO_4)_2{\cdot}6H_2O$ (11.1 mg, 0.03 mmol) was added and the mixture was allowed to stir for 24 h under ambient condition. Acetonitrile was partially evaporated under reduced pressure and 40 ml of dry diethyl ether was added to precipitate a light-green solid. The solid was isolated by filtration. Yield: 17.9 mg (52%). Anal. Calcd for $C_{38}H_{26}Cl_2CuN_8O_9$: C, 52.27; H, 3.00; N, 12.83; Cu, 7.28. Found: C, 52.89; H, 3.09; N, 13.07; Cu, 7.2. IR (cm^{-1}): $\nu_{N\text{–}H}$, 3203 and 3075; $\nu_{C=N}$, 1562; $\nu_{Hetaryl}$, 1458; ν_{ClO4}, 1103 and 1078. ESI-MS (positive ion mode, MeCN): m/z = 643.05 (89%, $[2(\mathbf{1}) - (H^+) + (Cu^{2+})]^+$). UV-vis in MeCN: λ, nm (ε, M $^{-1}$cm $^{-1}$): 395, 308, 281 (120,000).

[Cu(**2**)$_2(H_2O)](ClO_4)_2$. Yield: 71%. Anal. Calcd for $C_{38}H_{28}Cl_2CuN_{10}O_9$: C, 50.54; H, 3.12; N, 15.51; Cu, 7.04. Found: C, 50.92; H, 3.27; N, 15.23; Cu, 7.39. IR (cm^{-1}): $\nu_{N\text{–}H}$, 3076 and 2921; $\nu_{C=N}$, 1609; $\nu_{Hetaryl}$, 1485; ν_{ClO4}, 1093 and 1077; $\nu_{p\text{-}Aryl}$ 821 and 803. ESI-MS (positive ion mode, MeCN):

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m/z = 784.11 (98%, [2(**2**) +(Cu^{2+})+ (ClO_4^-)]$^+$). UV-vis in MeCN: λ, nm (ε, $M^{-1}cm^{-1}$): 356 (111,000), 310, 290.

[Cu(**3**)$_2$(H_2O)](ClO_4)$_2$. Yield: 80%. Anal. Calcd for $C_{58}H_{64}Cl_2CuN_{10}O_{13}S_4$: C, 50.78; H, 4.70; N, 10.21; Cu, 4.63. Found: C, 50,87; H, 4,10; N, 10,89; Cu, 4,21. IR (cm^{-1}): ν_{N-H}, 3366, 2917 and 2861; $\nu_{C=N}$, 1609; $\nu_{Hetaryl}$, 1484; ν_{ClO4}, 1093 and 1077; $\nu_{p\text{-}Aryl}$ 816 and 803; ν_{C-S}, 742. ESI-MS (positive ion mode, MeCN): m/z = 1255.05 (58%, [2(**3**) +(Cu^{2+})+ (ClO_4^-)]$^+$). UV-vis in MeCN: λ, nm (ε, $M^{-1}cm^{-1}$): 352 (109950), 282.

[Cu(**4**)$_2$(H_2O)](ClO_4)$_2$. Yield: 93%. Anal. Calcd for $C_{42}H_{34}Cl_2CuN_8O_{13}$: C, 50.79; H, 3.45; N, 11.28; Cu, 6.40. Found: C, 51.05; H, 3.87; N, 11.16; Cu, 6.5. IR (cm^{-1}): ν_{N-H}, 3366, 2917 and 2861; $\nu_{C=N}$, 1563; $\nu_{Hetaryl}$, 1491; ν_{OMe}, 1262 and 1228; ν_{ClO4}, 1093 and 1077. ESI-MS (positive ion mode, MeCN): m/z = 810 (58%, [2(**4**) + (Cu^{2+}) + (HO^-) + (H_2O)]$^+$. UV-vis in MeCN: λ, nm (ε, $M^{-1}cm^{-1}$): 450, 312, 279 (87,000)

[Cu(**5**)$_2$(H_2O)](ClO_4)$_2$. Yield: 37%. Anal. Calcd for $C_{54}H_{34}Cl_2CuN_8O_9S_4$: C, 53.98; H, 2.85; N, 9.33; Cu, 5.29. Found: C, 53.27; H, 2.70; N, 9.68; Cu, 5.36. IR (cm^{-1}): ν_{N-H}, 3366 and 2922; $\nu_{C=N}$, 1571; $\nu_{Hetaryl}$, 1488; ν_{ClO4}, 1093 and 1077; $\nu_{thiophene}$, 678. UV-vis in MeCN: λ, nm (ε, $M^{-1}cm^{-1}$): 370 (56,250), 312, 281, 265

Computational details

All computations were performed using the Gaussian 09 software package[42] by using the PBE1PBE functional.[43] In the calculation 6-31G(d) basis set was assigned to all elements with the exception of copper for which the Los Alamos effective core potentials plus the Double Zeta (LanL2DZ)[44] basis set were employed. Open-shell Cu(II) complexes were treated with a spin-unrestricted formalism. The geometric structures of the complexes in the ground state (doublet) were fully optimized without any symmetry restriction and vibration frequency calculations were performed to ensure that the optimized geometries represent local minima associated with positive eigenvalues only. This level of computation shows a very good agreement with experiment (see supplementary materials). Solvent effects were accounted for according to the experimental conditions. The solvation effects of acetonitrile were considered by using the polarizable continuum model by the integral equation formalism (IEFPCM)[45] with default convergence criteria. From ground stated optimized geometries, vertical electronic excitations were obtained with the time dependent density functional theory (TD-DFT) formalism[46,47] and the B3LYP, MPW1PW91 and M062X functionals. GaussSum[48-51] was used to display the absorption spectra and to calculate the fractional contributions of various groups to each molecular orbital.

Conclusions

The studied 1H-imidazo[4,5-*f*][1,10]phenanthrolines containing phenyl- (**1**), 4-(N,N-dimethylamino)phenyl- (**2**), 4-(azadithiacrown-ether)phenyl- (**3**) 3,4-dimethoxyphenyl- (**4**) and 2,2'-bithiophen-5-yl- (**5**) substituents demonstrate the complex formation with Cu(II) cations through the coordination of metal ions with phenantroline part of ligands. In case of 4-(azadithiacrown-ether)phenyl-1H-imidazo[4,5-*f*][1,10]phenanthroline the additional coordination of Cu(II) with crown ether fragments at the metal ion excess also occurs. The stable Cu(II) complex forms mixture of $\mathbf{L}_3{\cdot}Cu^{2+}$ and $\mathbf{L}_2{\cdot}Cu^{2+}$ complexes. When IPh ligand contains donor 4-(N,N-dimethylamino)phenyl-(**2**) or 4-(azadithiacrown-ether)phenyl- (**3**) substituents the autoreduction of Cu(II) to Cu(I) proceeds. The formation of $\mathbf{L}_2{\cdot}Cu^{2+}$ complex force a tetrahedral geometry about the copper atom and induces a positive shift in the reduction potential providing the occurrence of autoreduction of copper(II). The formed Cu(I) cations are stable in MeCN solution. Electrochemical study showed that the autoreduction is observed when Cu^{2+}/Cu^+ transfer and oxidation of ligand occur at the closed electrochemical condition. The potentials of oxidation of donor ligands 3,4-dimethoxyphenyl- and 2,2'-bithiophen-5-yl-1-H-imidazo[4,5-*f*][1,10]phenanthrolines (**4**, **5**) are substantial differ from the reduction potential of Cu^{2+}/Cu^+ transfer, in this case the Cu^{2+}/Cu^+ autoreduction has not been found.

The present studies have revealed the requirements for the occurrence of the process of Cu^{2+}/Cu^+ autoreduction demonstrating that how small changes in the molecular structure has a pronounced effect on the properties of metal complexes. This observation of a system, stabilizing both Cu(I) and Cu(II), is of interest in view of current studies of model compounds mimicking biological structure and redox properties.

Conflicts of interest

There are no conflicts to declare.

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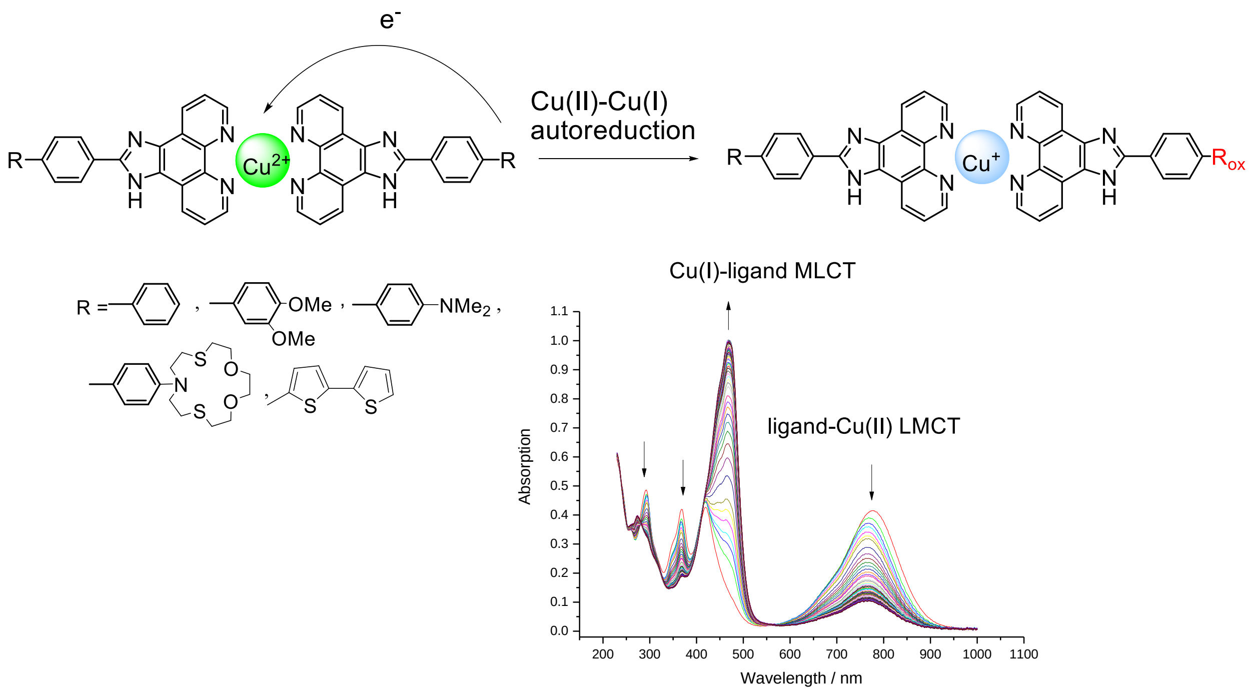
Intramolecular electron transfer in Cu(II) complexes with aryl-imidazo-1,10-phenanthroline derivatives: experimental and quantum chemical calculation studies

Olga A. Fedorova, Nikolai E. Shepel, Sergey D. Tokarev, Elena V. Lukovskaya, Yulia A. Sotnikova, Anna A. Moiseeva, Anthony D'Aléo, Frédéric Fages, François Maurel and Yury V. Fedorov



First observation of Cu(II)-Cu(I) autoreduction in complex with aryl-imidazo-1,10-phenanthroline derivatives