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Copper complexes formed by 3,5-bis(2,2'-bipyridin-4-ylethynyl)benzoic acid and its methyl and ethyl esters as studied by electrospray ionization mass spectrometry

Research Article

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Abstract: Electrospray ionization mass spectrometry was used to study the complexes of ligands containing two bipyridine units, namely 3,5-bis(2,2-bipyridin-4-ylethynyl)benzoic acid (1) and its methyl and ethyl esters (2, 3), with copper cation, with $CuCl_2$ as a source of copper. It was found that the type of complexes formed strongly depends on $CuCl_2$ concentration. At lower $CuCl_2$ concentration, the detected complexes were rather simple and some of them were formed upon electrospray ionization conditions e.g. ions $[2_2+Cu_2]^{2+}$ and $[3_2+Cu_2]^{2+}$ (complexes ligand-Cu(I) of stoichiometry 2:2) which are analogical to the well known, for quaterpyridine, helical complexes. At higher $CuCl_2$ concentration, the detected complexes were more complicated, and most of them contained copper cations bridged by chlorides. The largest ions were $[L_2+Cu_4Cl_6]^{2+}$. The CID MS/MS spectra of these ions allowed determination of their mass spectrometric fragmentation pathways and as a consequence their structure elucidation.

Keywords: *Bipyridine • Copper complexes • Electrospray ionization mass spectrometry*

1. Introduction

2,2'-Bipyridine (bipy) is a well known organic ligand which forms particularly stable complexes with transition metal cations. Among the bipy-metal complexes, bipy-Cu complexes have attracted notable attention. In this year alone more than 10 papers on the complexes containing copper cation chelated by bipy or its conjugates have already appeared [1-11]. On the other hand, copper complexes with organic compounds containing two (or more) bipy units are not so numerous. The simplest compounds containing two bipy units,quarterpyridine and its copper complexes, were studied in details [12-16]. There are a few other examples of copper complexes with compounds containing two (or more) bipy units [17-26].

Recently we have synthesized organic ligand which contains two bipy units namely 3,5-bis(2,2-bipyridin-4-ylethynyl)benzoic acid - compound **1** [27]. Upon its preparation, its esters (methyl- **2** or ethyl - **3**) were also obtained (Scheme 1).

Structure of **1**-**3** does not allow a coordination of one metal cation by two bipy units originating from one ligand **1**-**3**. Obviously, metal cation coordinated by bipy unit from one ligand can be also coordinated by bipy unit from another ligand or by the counter ion. Thus, theoretically a number of copper complexes can be expected for **1**-**3**. In this work we used electrospray ionization mass spectrometry (ESI-MS) to identify what kinds of copper complexes, *i.e.*, ligands **1**-**3** are able to form. As a source of copper cations we used $CuCl_2$. It is well known that ESI-MS is a very good tool allowing detection of

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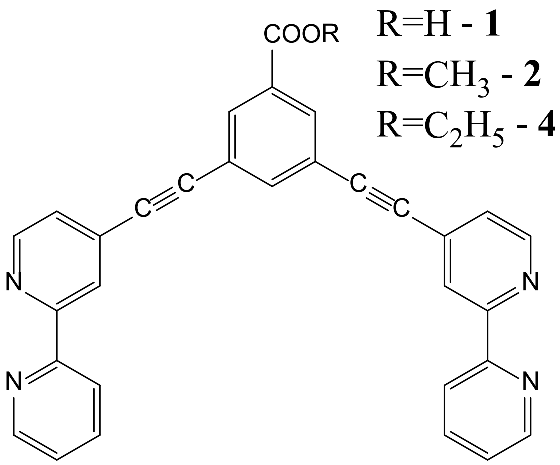


Scheme 1. Structure of 3,5-bis(2,2-bipyridin-4-ylethynyl)benzoic acid - compound **1** and its methyl and ethyl esters (**2** and **3**).

metal-organic ligand complexes [28-34]. It is generally accepted, that ESI mass spectra of solutions containing metal complexes with organic ligands, at least from the qualitative point of view, well reflect the species present in solution [35-37].

2. Experimental procedure

ESI mass spectra were obtained on a Waters/Micromass (Manchester, UK) ZQ2000 mass spectrometer (single quadrupole type instrument, Z-spray, software MassLynx V3.5). The sample solutions were infused into the ESI source using a syringe pump, the flow rate was 80 mL min^{-1}. The ESI source potentials were capillary 3 kV, lens 0.5 kV, extractor 4 V and cone voltage (CV) 10-50 V. Cone voltage has the most profound effect on the mass spectra obtained. Increase in this parameter led to the so called “in-source” fragmentation/dissociation but a too low cone voltage could cause a decrease in sensitivity. The source temperature was 120°C and the desolvation temperature was 300°C. Nitrogen was used as the nebulising and desolvating gas at the flow-rate of 100 and 300 l h^{-1}, respectively.

MS/MS spectra were taken on a Waters/Micromass (Manchester, UK) Q-tof Premier mass spectrometer (software MassLynx V4.1, Manchester, UK). The sample solutions were infused into the ESI source by a syringe pump at a flow rate of 5 mL min^{-1}. The electrospray voltage was 2.7 kV and the cone voltage - 30 V. The source temperature was 80°C and the desolvation temperature was 250°C. Nitrogen was used as the cone gas and desolvating gas at the flow-rates of 50 and 800 L h^{-1}, respectively. Argon was used as a collision gas at the flow-rate 0.5 mL min^{-1} in the collision cell. Collision energy, the most important parameter for MS/MS experiments, was 5-30 eV.

3. Results and discussion

A large number of ESI mass spectra was obtained (at different ligand and metal concentration and different cone voltages), obviously only representative examples will be shown and discussed. At first, the complexes detected for solutions containing $CuCl_2$ and ligand at the same concentrations (2×10^{-5} mol dm^{-3}) will be discussed and then the complexes detected for solutions containing excess of copper (ligand concentration 2×10^{-5} mol dm^{-3}, $CuCl_2$ concentration 6×10^{-5} mol dm^{-3}). When analyzed solutions contained less $CuCl_2$ than ligand, the complexes were characterized by very low abundances.

3.1. Solutions containing equal copper and ligand concentrations

For a solution containing copper and ligand at the same concentrations the most abundant ions corresponded to the protonated ligand molecules (Fig. 1). Copper complexes were also detected.

For all three ligands there were ions [**L**$_2$+Cu]$^+$ and [**L**$_2$+CuCl]$^+$ (**L** stands for a neutral ligand molecule). For all ligands doubly charged ions were detected, for ligand **2** and **3 -** ions [**2**$_2$+Cu$_2$]$^{2+}$ and [**3**$_2$+Cu$_2$]$^{2+}$, whereas for ligand **1 -** ion [**1**$_2$+Cu$_2$Cl$_2$]$^{2+}$. It has to be stressed that ions [**2**$_2$+Cu$_2$]$^{2+}$ and [**3**$_2$+Cu$_2$]$^{2+}$ (complexes ligand-Cu(I) of stoichiometry 2:2) are analogous to the well known for quaterpyridine, helical complexes [12-16].

High abundances of ions [**1**$_2$+CuCl]$^+$ and [**1**$_2$+Cu$_2$Cl$_2$]$^{2+}$ indicate that complex Cu-**1** is prone to attach a chloride anion, in contrast to Cu-**2** and Cu-**3** complexes (although it is difficult to rationalize). Doubly charged ions ([**1**$_2$+Cu$_2$Cl$_2$]$^{2+}$, [**2**$_2$+Cu$_2$]$^{2+}$, [**3**$_2$+Cu$_2$]$^{2+}$) were detected at low cone voltages, at higher cone voltages they dissociate and we obtain singly charged ions [**1**+CuCl]$^+$, [**2**+Cu]$^+$, [**3**+Cu]$^+$. The singly/doubly charged ions which have the same m/z value can be differentiated by their characteristic isotope patterns [14], as demonstrated for ions [**1**$_2$+Cu$_2$Cl$_2$]$^{2+}$ and [**1**+CuCl]$^+$ in Fig. 2. Ion [**1**$_2$+Cu$_2$Cl$_2$]$^{2+}$ can be regarded as a dimer of ion [**1**+CuCl]$^+$ and a plausible structure of ion [**1**$_2$+Cu$_2$Cl$_2$]$^{2+}$ is shown in Scheme 2. Two copper cations are bridged by two chlorides and each of the copper cation has the coordination number of 4.

Ions [**L**$_2$+CuCl]$^+$ and [**1**$_2$+Cu$_2$Cl$_2$]$^{2+}$ contain Cu(II) and can exist in solution, whereas ions [**L**$_2$+Cu]$^+$ and

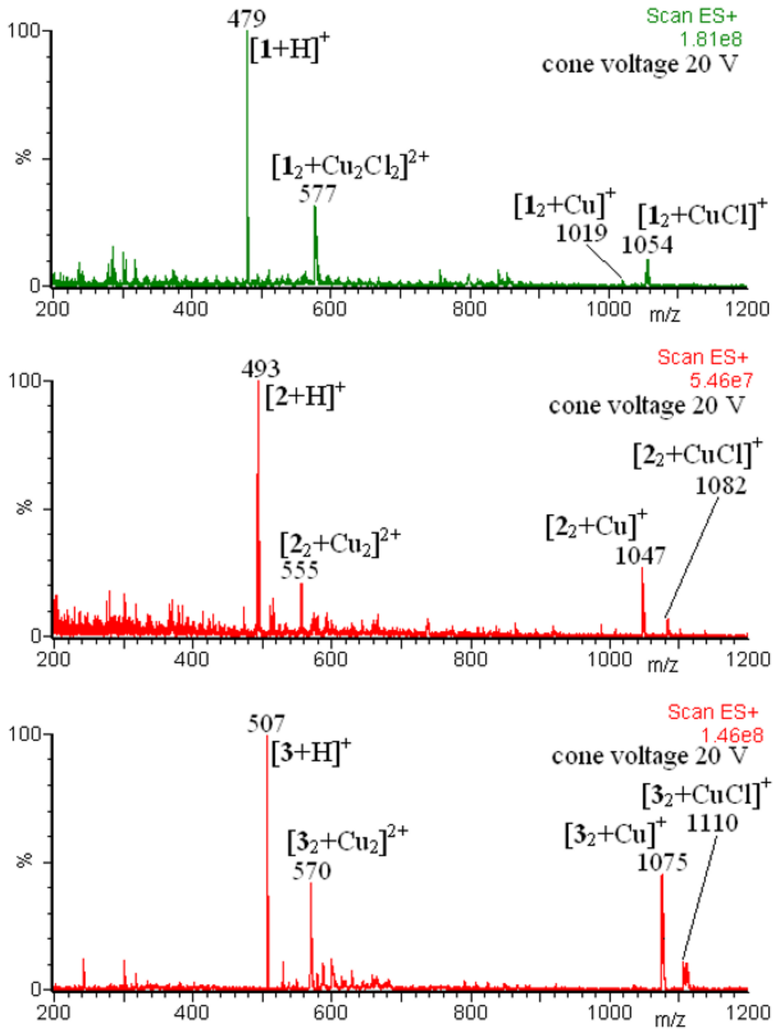
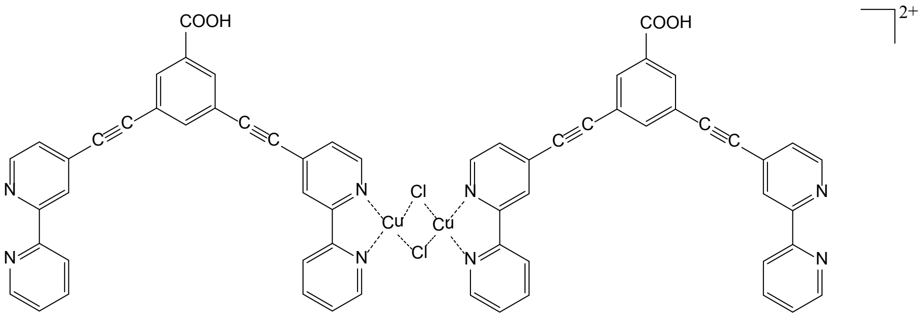


Figure 1. ESI mass spectra of solutions containing equal copper and ligand concentrations.



Scheme 2. Plausible structure of ion $[1_2+Cu_2Cl_2]^{2+}$.

$[\mathbf{2}_2+Cu_2]^{2+}$ and $[\mathbf{3}_2+Cu_2]^{2+}$ contain Cu(I) and they are formed in ESI conditions. It is worth noting that there are no doubly charged ions $[\mathbf{L}_2+Cu]^{2+}$ (maybe they are easily reduced upon ESI process to ions $[\mathbf{L}_2+Cu]^{+}$). Ions $[\mathbf{L}_2+Cu]^{+}$ can be also formed from ions $[\mathbf{L}_2+CuCl]^{+}$ by loss of a chlorine atom. However, in the CID MS/MS spectra of ions $[\mathbf{L}_2+CuCl]^{+}$ it was not observed. The decomposition of ions $[\mathbf{L}_2+CuCl]^{+}$ consists of the loss of a neutral ligand molecule producing ions $[\mathbf{L}+CuCl]^{+}$, as shown in Fig. 3 for ion $[\mathbf{3}_2+CuCl]^{+}$.

The easy loss of neutral ligand molecule from ions $[\mathbf{L}_2+CuCl]^{+}$ indicates that in these ions copper cations are not strongly bound by two bipy units (originated from two ligand molecules). Ions $[\mathbf{L}_2+CuCl]^{+}$ can be regarded

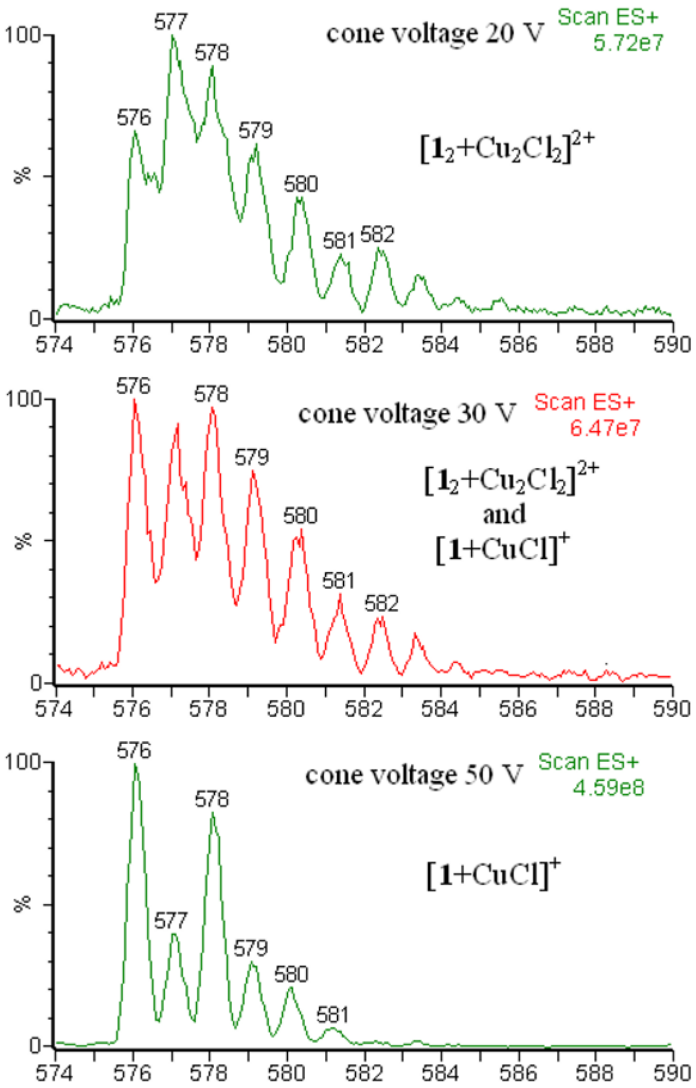


Figure 2. Isotope patterns of ions $[1_2+Cu_2Cl_2]^{2+}$ and $[1+CuCl]^{+}$ (obtained at low resolution mass spectrometer).

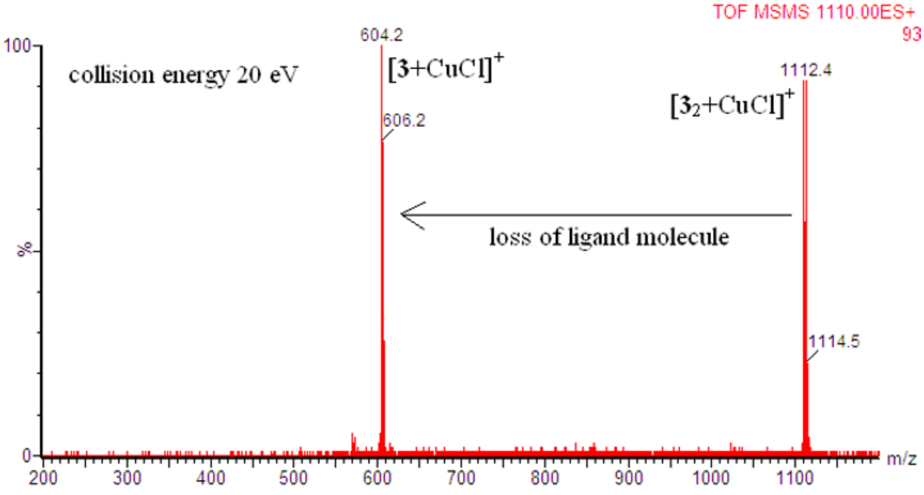


Figure 3. CID MS/MS spectrum of ion $[3_2+CuCl]^{+}$.

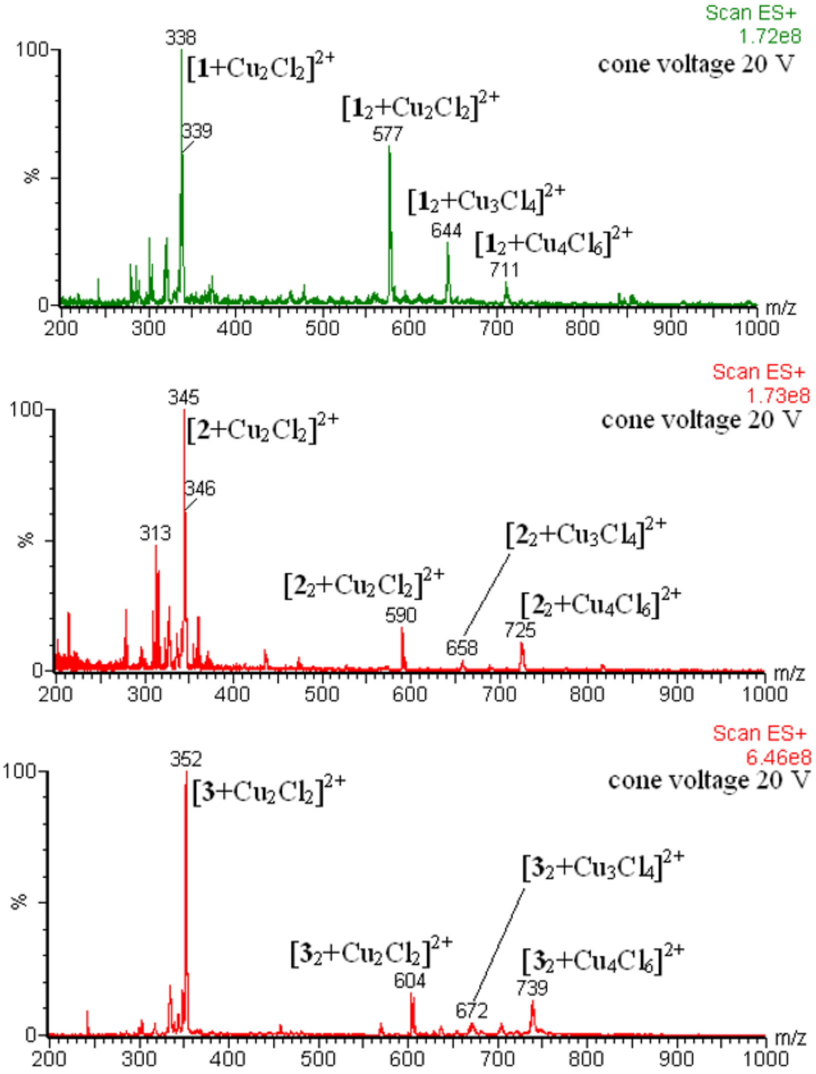


Figure 4. ESI mass spectra of solution containing one of the ligand and excess of copper.

as an adduct between $[\mathbf{L}+CuCl]^+$ and **L** molecule (the second **L** molecule is loosely bound).

The complexes detected for solution containing copper and ligand at the same concentrations are rather simple and it does not seem to be necessary to discuss them in detail, *e.g*. their structures. More interesting complexes were detected for the solutions containing excess of copper.

3.2. Solutions containing excess of copper

For the solution containing excess of copper the most abundant were doubly charged ions $[\mathbf{L}+Cu_2Cl_2]^{2+}$ (Fig. 4). Other detected ions were $[\mathbf{L}+Cu_2Cl_2]^{2+}$, $[\mathbf{L}_2+Cu_3Cl_4]^{2+}$ and $[\mathbf{L}_2+Cu_4Cl_6]^{2+}$. All ions contained Cu(II) thus they can exist in solution.

The characteristic isotopic patterns confirmed the compositions of the ions (Fig. 5), and enabled also differentiation of ions of the same m/z, namely $[\mathbf{L}_2+Cu_4Cl_6]^{2+}$ and $[\mathbf{L}+Cu_2Cl_3]^{+}$ (the latter was not detected at all).

The question of interest is the structure of the detected ions $[\mathbf{L}+Cu_2Cl_2]^{2+}$, $[\mathbf{L}_2+Cu_3Cl_4]^{2+}$ and $[\mathbf{L}_2+Cu_4Cl_6]^{2+}$. It is reasonable that ions $[\mathbf{L}+Cu_2Cl_2]^{2+}$ have the structure shown in Scheme 3. Each of the two chlorides is attached to one of the two copper cations (attachment of two chlorides to one copper cation seems to be less probable for ion $[\mathbf{L}+Cu_2Cl_2]^{2+}$).

For ions $[\mathbf{L}_2+Cu_4Cl_6]^{2+}$ there is only one logical structure, shown in Scheme 4. Two “central” copper cations are bridged by two chlorides and each of the copper cation has the coordination number of 4.

More difficult is to propose the structure of ions $[\mathbf{L}_2+Cu_3Cl_4]^{2+}$. There are two most logical possibilities, **a** and **b**, Scheme 5.

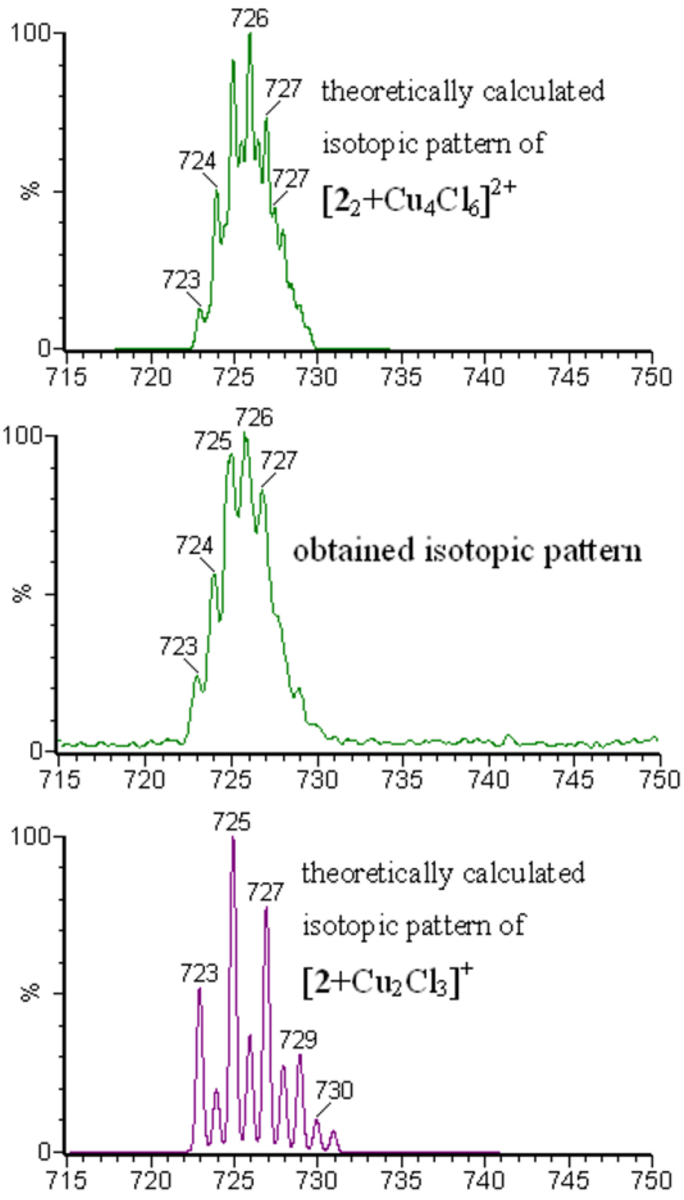
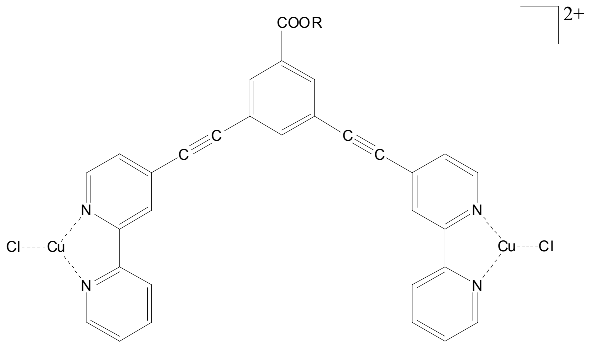


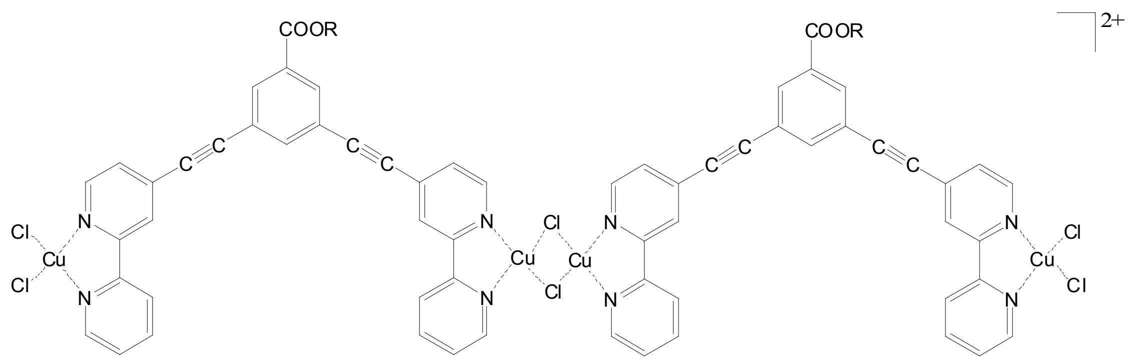
Figure 5. Comparison of the obtained isotopic pattern with theoretically calculated isotopic patterns of $[2_2+Cu_4Cl_6]^{2+}$ and $[2+Cu_2Cl_3]^+$ (for low resolution mass spectrometer).



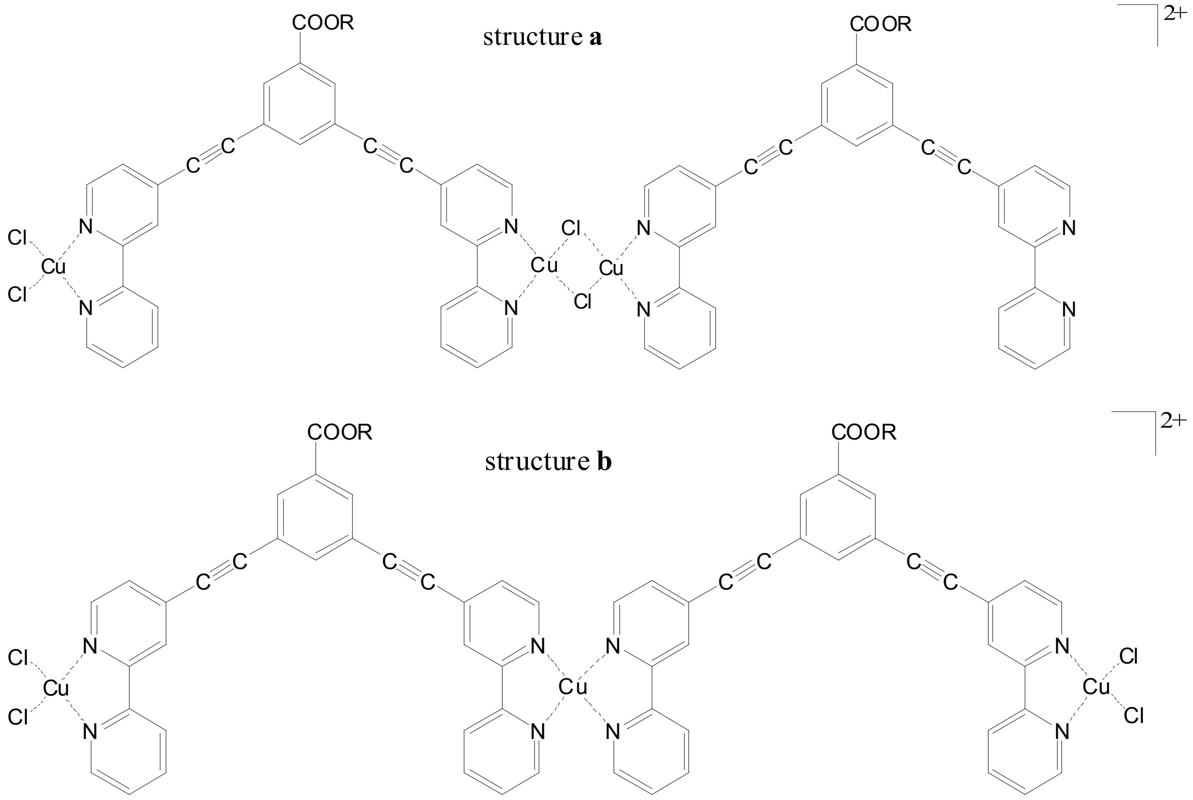
Scheme 3. Reasonable structure of ions $[L+Cu_2Cl_2]^{2+}$.

Structure **b** seems to be less favoured since it contains Cu(II) strongly coordinated by two bipy units and similar complexes were not detected for solution containing copper and ligand at the same concentrations. Structure **a** seems to be more probable, it can be formed from ions $[\mathbf{L}_2+Cu_4Cl_6]^{2+}$ by loss of $CuCl_2$ molecule. The CID MS/MS spectra of ions $[\mathbf{L}_2+Cu_4Cl_6]^{2+}$ confirmed it. As shown in Fig. 6 for ion $[\mathbf{3}_2+Cu_4Cl_6]^{2+}$, the loss of $CuCl_2$ molecule from ion $[\mathbf{3}_2+Cu_4Cl_6]^{2+}$ is observed producing ion $[\mathbf{3}_2+Cu_3Cl_4]^{2+}$.

There is also the loss of the second $CuCl_2$ molecule, in other words ions $[\mathbf{L}_2+Cu_3Cl_4]^{2+}$ also lose $CuCl_2$ molecule. The CID MS/MS spectrum of ion $[\mathbf{3}_2+Cu_3Cl_4]^{2+}$ at lower



Scheme 4. Reasonable structure of ions $[L_2+Cu_4Cl_6]^{2+}$.



Scheme 5. Two possible structures (a and b) of ions $[L_2+Cu_3Cl_4]^{2+}$.

collision energy revealed the loss of $CuCl_2$ molecule producing ion $[\mathbf{3}_2+Cu_2Cl_2]^{2+}$ (Fig. 7, top), whereas at higher collision energy the loss of $CuCl_2$ molecule was followed by dissociation of ion $[\mathbf{3}_2+Cu_2Cl_2]^{2+}$ producing singly charged ion $[\mathbf{3}+CuCl]^+$ (Fig. 7, bottom). Ions $[\mathbf{3}_2+Cu_2Cl_2]^{2+}$ and $[\mathbf{3}+CuCl]^+$ have identical m/z value but they are easily differentiated by different isotopic patterns.

Ions $[\mathbf{L}_2+Cu_4Cl_6]^{2+}$ were the largest complexes detected for ligands **1**-**3**. On the grounds of the CID MS/MS spectra shown in Figs. 6 and 7 the mass spectrometric fragmentation pathway of ions $[\mathbf{L}_2+Cu_4Cl_6]^{2+}$ were determined, as shown in Scheme 6, which is in agreement with the proposed structures of the ions discussed.

4. Conclusions

The ligands containing two bipy units, namely 3,5-bis(2,2-bipyridin-4-ylethynyl)benzoic acid (**1**) and its esters (**2**, **3**) are able to form a number of complexes

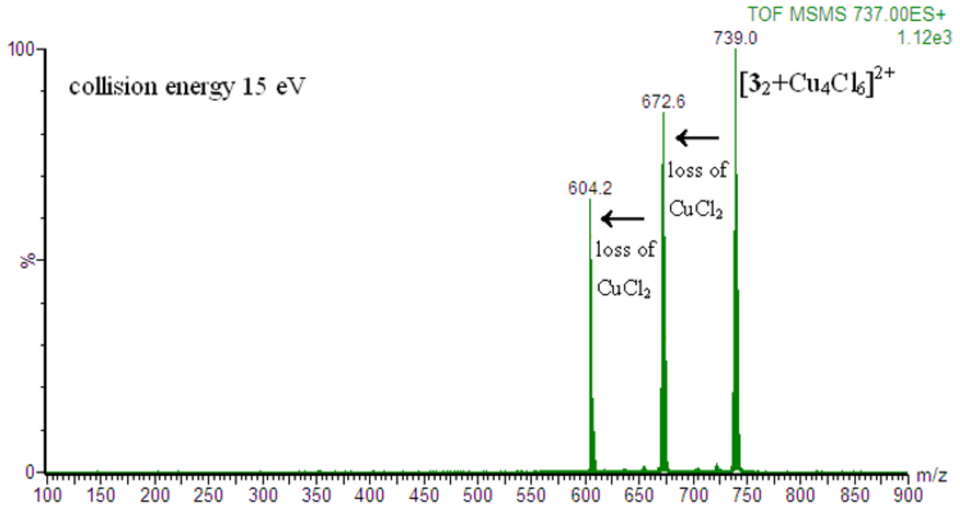


Figure 6. CID MS/MS spectrum of ion $[3_2\text{+}Cu_4Cl_6]^{2+}$.

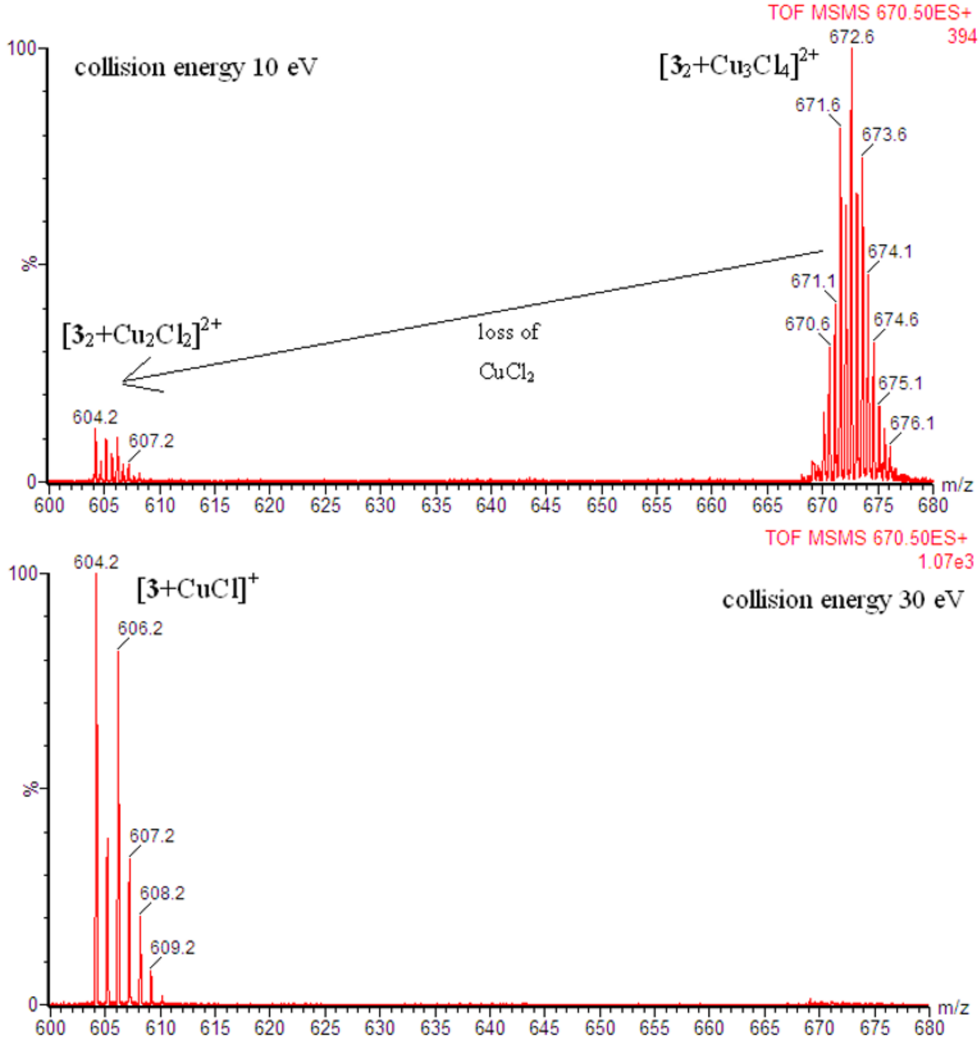
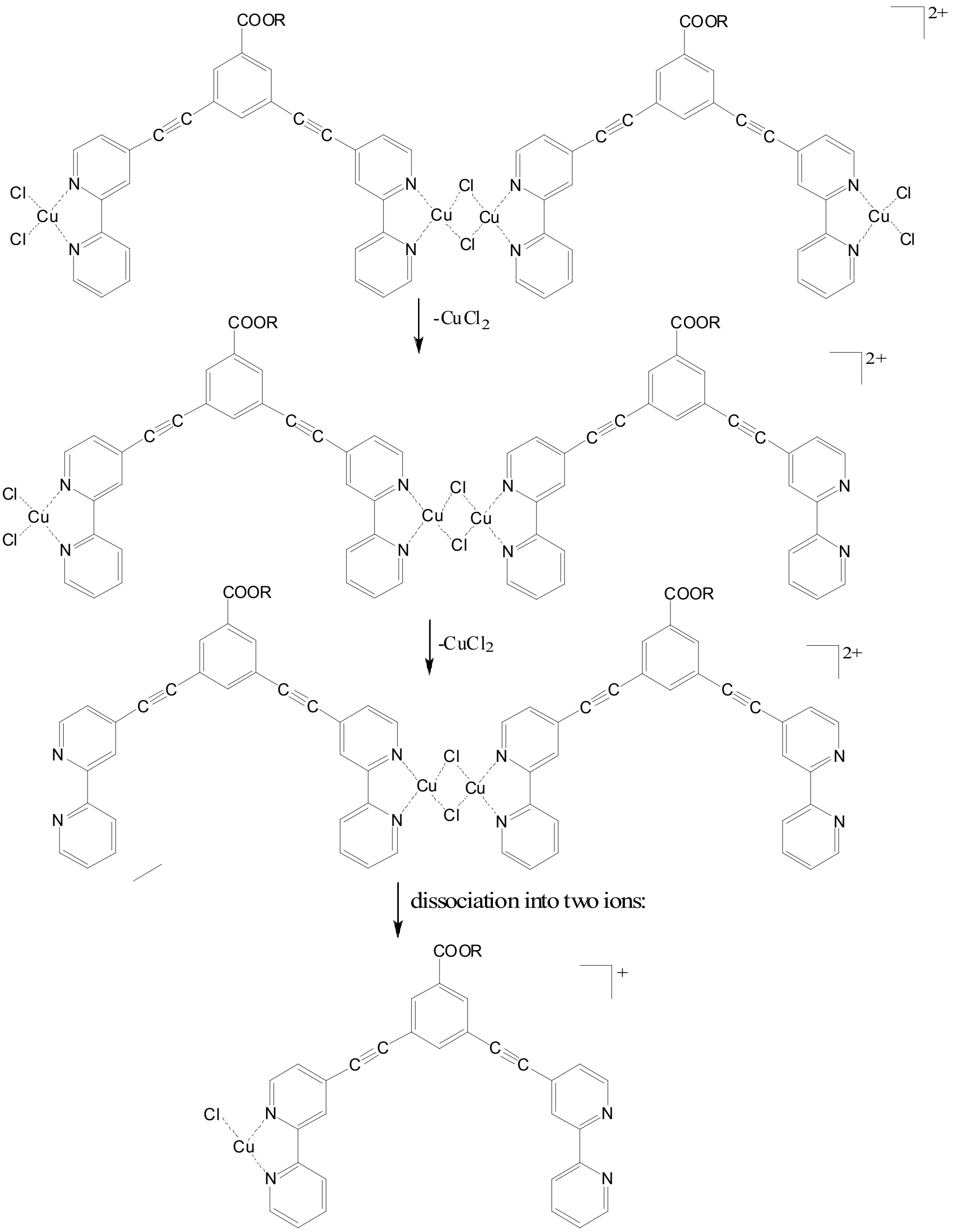


Figure 7. CID MS/MS spectra of ion $[3_2\text{+}Cu_3Cl_4]^{2+}$ obtained at different collision energies.



Scheme 6. Mass spectrometric fragmentation pathway of ions $[L_2+Cu_4Cl_6]^{2+}$.

of different types with copper cation, when using $CuCl_2$ as a source of copper (although the ions containing Cu^{2+} coordinated by two bipy units were not detected). At lower $CuCl_2$ concentration, the detected complexes were rather simple and some of them were formed in upon electrospray ionization, *e.g.* ions $[\mathbf{2}_2+Cu_2]^{2+}$ and $[\mathbf{3}_2+Cu_2]^{2+}$ (complexes ligand-Cu(I) of stoichiometry 2:2) which are analogical to the helical complexes well known for quaterpyridine. There was also ion $[\mathbf{1}_2+Cu_2Cl_2]^{2+}$ which contains copper cations bridged by two chlorides. At higher $CuCl_2$ concentrations, the detected complexes were more complicated, and most of them contained copper cations bridged by chlorides. The largest ions were $[\mathbf{L}_2+Cu_4Cl_6]^{2+}$. Upon CID conditions, these ions successfully lose two $CuCl_2$ molecules and then dissociate into singly charged $[\mathbf{L}+CuCl]^{+}$ ion. Mass spectrometric decomposition of ions $[\mathbf{L}_2+Cu_4Cl_6]^{2+}$ enabled structure elucidation of the ions discussed.

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