

Article

The Copper(II) Ions Solvent Extraction with a New Compound: 2,6-Bis(4-Methoxybenzoyl)-Diaminopyridine

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Abstract: A new compound 2,6-bis(4-methoxybenzoyl)-diaminopyridine (L) was used as an extractant for copper(II) ion recovery in a solvent extraction conducted at a temperature of 25 °C. The best results (99% recovery of copper(II) ions) were obtained when the aqueous phase contained 0.001 mol/dm³ Cu(II) and 0.2 mol/dm³ NH₃ (pH~5.8), while the organic phase was a 0.001 mol/dm³ chloroform solution of 2,6-bis(4-methoxybenzoyl)-diaminopyridine. Spectrophotometry studies were used to determine the dissociation constant of the tested compound and determine the stability constant of the complex of subjected compound with copper(II) ions. The high-resolution mass spectrometry (HRMS) and higher energy collisional dissociation tandem mass spectrometry (HCD MS/MS) methods have been applied for the confirmation of the structure of 2,6-bis(4-methoxybenzoyl)-diaminopyridine and to determine its complexation with Cu(II) in solution.

Keywords: solvent extraction; 2,6-bis(4-methoxybenzoyl)-diaminopyridine; dissociation constant; stability constant; mass spectrometry

1. Introduction

There are many separation processes of metal ions from water solutions. One of the most often used is the solvent extraction. Applications of liquid-liquid extraction can be found in industries such as petrochemical, pharmaceutical and hydrometallurgical. Hydrometallurgy helps concentrate metals like zinc or copper, for electrowinning as well as for separating the complex metallic system, for example, nickel/cobalt and other metal ions [1]. This method can be used for the selective separation of other metal ions: Zn(II), Cd(II), Al(III), Co(II), Ni(II) [2–6] or Cu(II) [7,8]. The copper is widely used in the industry because of its properties, therefore it can be found in electrical materials, construction, transport and industrial machines [9]. The recovery of copper(II) ions is very important for environmental protection. Copper belongs to not biodegradable metals. This metal has a tendency to accumulate in animals and humans organism, causing various diseases and disorders [10]. As a result of the application of copper in the industry its ions are present in the wastewaters and waste solutions originating from the electronic, electroplating etc. [11]. Therefore, the recovery of copper(II) ions is the subject of many studies, because copper salts are cheap and easy to obtain as well as being less dangerous than salts of other transition metals [12]. For this purpose various methods such as precipitation, coagulation, adsorption, ion exchange, membrane separation and solvent extraction are used [2].

In the extraction process, we used organic solvents and an extractant. The main success of the extraction processes is determined by the selection of an appropriate extractant [13], which from the economical point of view would be able to recovery at least 90% of metal ions from the treated water solutions. Nowadays, the common extractants for copper(II) that are available commercially are expensive. Therefore, new extractants are constantly being searched for.

In literature a lot of information can be found about aminopyridines. This group of compounds can create complexes with transitional metal ions. For example, ions like Cu(II), Zn(II), Co(II) and Cd(II) can participate in the formation of macrocyclic complexes with 2,6-diaminopyridine [14]. There are known complexes of Schiff-base macrocyclic ligands. Ilhan et al. composed a new compound of 2,6-diaminopyridine and 1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane [15], and 2,6-diaminopyridine and 1,6-bis(2-formylphenyl) hexane [16] and characterized their complexes. Presented examples prove the high affinity of these compounds to metal ions. Nonetheless, there is little information about metals recovery using aminopyridines. Zhai et al. were some of the first to investigate the selective magnetic extraction of copper and zinc ions in solid phase using modified silica coated Fe₃O₄ nanoparticles with 2,6-diaminopyridine. They obtained high extraction efficiencies [17].

The results obtained in the referenced articles inspired us to attempt to use a derivative of 2,6-diaminopyridine for metal ions extraction from aqueous solutions.

In this paper for the first time a 2,6-bis(4-methoxybenzoyl)-diaminopyridine (C₂₁H₁₉N₃O₄) derived from 2,6-diaminopyridine was used as new extractant for copper(II) ions recovery. This work aimed to check the ability of this compound to be used in the solvent extraction process.

To achieve this aim, the structure of the obtained compound should be known and its complexation with copper(II) in solution measured. Moreover, the dissociation constant of the studied compound and constant stability of L: Cu²⁺ should be determined.

2. Materials and Methods

2.1. Synthesis and Properties of 2,6-Bis(4-Methoxybenzoyl)-Diaminopyridine

The structure of the compound 2,6-bis(4-methoxybenzoyl)-diaminopyridine (L) used in the studies is shown in Figure 1. All the substrates for the synthesis of 2,6-bis(4-methoxybenzoyl)-diaminopyridine were purchased from Sigma-Aldrich and used without further purification. The synthesis procedure consisted of the following steps: (a) to the magnetically stirred solution of 2,6-diaminopyridine (Sigma Aldrich, Poznań, Poland) and triethylamine (Sigma Aldrich, Poznań, Poland) in dry tetrahydrofuran (THF) (Avantor, Gliwice, Poland) (at 4 °C) the 4-methoxybenzoyl chloride (Sigma Aldrich, Poznań, Poland) was added (solution in dry THF) dropwise (15 min), (b) the mixture was stirred overnight, evaporated and treated with chloroform and water mixture, (c) the chloroform (Avantor, Gliwice, Poland) layer was separated, washed with water, dried with MgSO₄ (Avantor, Gliwice, Poland) and evaporated, and (d) the residue was recrystallized from THF/hexane. The method of the synthesis has been described in detail elsewhere [18].

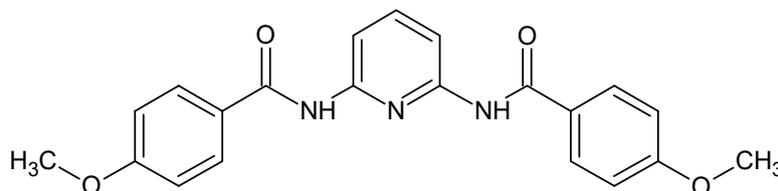
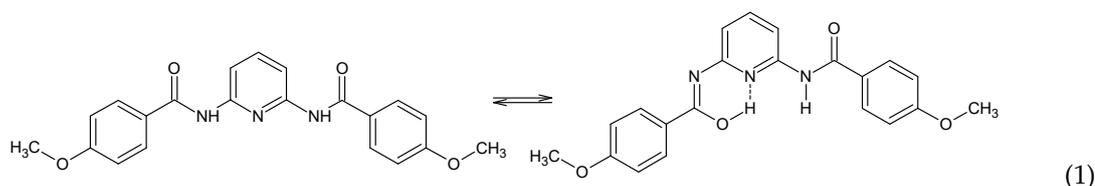


Figure 1. Structure of compound 2,6-bis(4-methoxybenzoyl)-diaminopyridine (C₂₁H₁₉N₃O₄).

The presence of NH group between two electron acceptors (C=O and pyridine ring) in the obtained compound (L) approaches it to the β-diketone molecule [19] in the light of its tautomerism. That is

why the studied compound can probably undergoes tautomerism according to Equation (1) [20]. The obtained enol form may be stabilized by intramolecular hydrogen bonding.



2.2. Other Reagents

The copper(II) nitrates, both of analytical reagent grade (Avantor, Gliwice, Poland) were recrystallized from distilled water. The concentration of the potassium nitrate solution was determined gravimetrically as potassium sulphate, whereas the concentration of the aqueous copper ion solutions were standardized by titration using EDTA solution or by the atomic absorption spectrometry method. Nitric acid (analytical reagent grade was obtained from Avantor Company, Gliwice, Poland) was standardized against anhydrous sodium carbonate. Ammonia was obtained from Avantor, Gliwice, Poland (analytical reagent grade). Carbonate free potassium hydroxide (the titrant, Avantor, Gliwice, Poland) was prepared and standardized against a standard potassium hydrogen phthalate solution. Chloroform and methanol (analytical reagent grade, Avantor, Gliwice, Poland) were used as received. The pH-meter was calibrated using commercial technical buffer solutions (Mettler Toledo, Greifensee, Switzerland) having a pH of 2.00, 4.01, 7.00, and 10.00.

2.3. Mass Spectrometry

All mass spectrometry experiments were performed on the Q-Exactive Orbitrap mass spectrometer (Thermo Scientific, Bremen, Germany). Samples of the compound 2,6-bis(4-methoxybenzoyl)-diaminopyridine (L) and $\text{Cu}(\text{NO}_3)_2$ (Avantor, Gliwice, Poland) were dissolved in methanol (Avantor, Gliwice, Poland) and distilled water (1:1) respectively, to a concentration of 1 mmol/dm^3 . Analytical solutions of L and metal salt were prepared (1:1, 1:4 and 1:10) in methanol to give a final concentration of 10 mmol/dm^3 , before being introduced into the mass spectrometer using an electrospray source. Data acquisition and analysis were conducted using the Xcalibur (Thermo Xcalibur 4.1.31.9, Waltham, USA) software. All mass spectra were obtained with a resolution of 70,000 at m/z 200. HCD MS/MS experiments were performed with nitrogen gas (gas generator NiGen LCMS 40-1, Tremezzina, Italy) at a normalized collision energy of 35%.

2.4. Dissociation Constant (pK_a) of 2,6-Bis(4-Methoxybenzoyl)-Diaminopyridine

The dissociation constant (pK_a) of 2,6-bis(4-methoxybenzoyl)-diaminopyridine (L) was determined by the spectrophotometric method. Solution of (L) in methanol with a concentration of 0.0011 mol/dm^3 was prepared. Then the 11 solutions were prepared to spectrophotometric measurements in this way that to appropriate amount of the stock solution was added an appropriate amount of one of the commercial technical buffer solution (Mettler Toledo, Greifensee, Switzerland) having a pH of 2.00, 4.01, 7.00, 9.21 or 10.00. For absorption measurements a wavelength of 264 nm was used.

2.5. Determination of Cu-Ligand Stability Constant

To calculate the stability constant of the complex of copper(II) ions with ligand (2,6-bis(4-methoxybenzoyl)-diaminopyridine) it was necessary to record their absorption spectra. For this purpose, a stock solution of copper ions with a concentration of 0.0016 mol/dm^3 and solution of ligand in methanol ($2.65 \cdot 10^{-5} \text{ mol/dm}^3$) were made. Then the appropriate amounts of copper ion solution and methanol solution of the ligand were mixed to prepare samples for a spectrophotometric analysis. The absorption spectra of the prepared samples were recorded on Cary 50 spectrophotometer

(Varian, Melbourne, Victoria, Australia) with varying molar ratios of the components (L: cation). The spectra were recorded in the range of the wavelength 200 to 450 nm.

2.6. Extraction Procedure

The measurements were run at 25 °C and a fixed ionic strength maintained in the aqueous phase with 0.5 mol/dm³ solution of potassium nitrate. The aqueous phase contained 0.001 mol/dm³ Cu(II) ions and 0.2 mol/dm³ NH₃ (pH~5.8), the organic phase contained 0.001 mol/dm³ ligand in chloroform. Ammonia was used for pH adjustment during the extraction process. Copper hydroxide starts to precipitate in pH~7.5.

A 4.5 cm³ of aqueous phase was introduced to each of the five graduated test tubes. Then a chloroform solution of (L) was added to each test tube, in this way that the volume of the organic phase was always equal to the volume of the aqueous phase but the concentration of the ligand was varied in the range from 0.0001 to 0.001 mol/dm³ (samples I-V). The prepared samples were then shaken for one hour. The equilibrium was established after approximately 15 min. It was checked to see if any changes in the phase volumes had occurred, then the phases were separated and the pH of the aqueous phase was measured. The Cu(II) concentration in the aqueous phase was determined by atomic absorption spectrophotometry (AAS 240FS Spectrometer, Agilent, Santa Clara, CA, USA).

3. Results and Discussion

3.1. Characterization of 2,6-Bis(4-Methoxybenzoyl)-Diaminopyridine and Its Complexation with Cu(II) by Mass Spectrometry Methods

The structure of 2,6-bis(4-methoxybenzoyl)-diaminopyridine (L) and its ability to form complexes with copper(II) ions in solution was confirmed by application of the electrospray ionization high-resolution mass spectrometry (ESI HRMS) and higher energy collisional dissociation tandem mass spectrometry (HCD MS/MS) methods. ESI is a soft ionization technique, which enables most of the small molecules analyzed to be transferred directly from the solvent into the mass spectrometer without change in their structures [21]. HRMS methods, based on measurement of the mass-to-charge ratio (m/z) of the analyte ions in the gas phase were characterized by high mass accuracy and sensitivity, which were necessary for the precise determination of the elemental composition and charge of the ions formed. HCD tandem mass spectrometry method, which is variation of traditional collision induced dissociation technique (CID), enabled the controlled decomposition of selected ions of a given chemical compound into smaller fragments (as a result of inelastic collisions of ions with inert gases). Analysis of the resulting fragmentation products provided information about the structure of analyte ions [22].

Electrospray ionization of the solution containing 2,6-bis(4-methoxybenzoyl)-diaminopyridine (L) led to the formation of singly charged ions $[L+H]^+$ ($C_{21}H_{20}N_3O_4$, $m/z_{meas} = 378.1440$, $m/z_{calc} = 378.1453$) of the analyzed compound. HCD of $[L+H]^+$ ions led to the formation of a series of products, some of which were generated as a result of intramolecular rearrangements. Figure 2 shows the proposed $[L+H]^+$ ions HCD fragmentation pathways and chosen products structures. However, for some of the generated products, in addition to the structures shown in Figure 2 other ways of combining the atoms in the molecules should also be considered (for example structures differing by the location of the OH group attached to the pyridine ring in $[C_{13}H_{12}O_3N_2+H]^+$ or by the location of the charge in $[C_{13}H_{11}O_2N_2]^+$). It cannot be excluded that some of the generated products result from secondary fragmentation reactions.

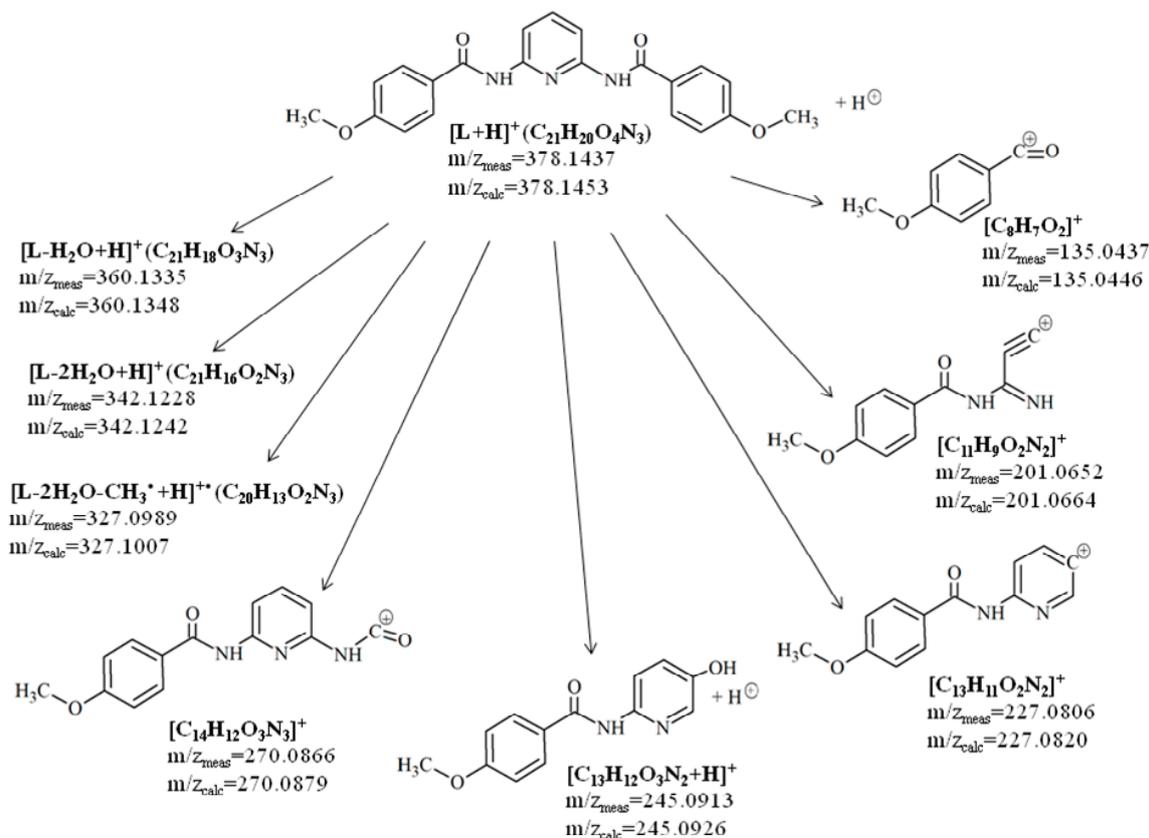


Figure 2. Proposed $[L+H]^+$ ions higher energy collisional dissociation (HCD) fragmentation pathways and products structures.

Detailed analysis of the fragmentation processes is not the subject of this work but the results of ESI HCD MS/MS experiments performed for singly charged ions $[L+H]^+$, allow for confirmation of the structure of the L compound. In comparison with conventional structure confirmation methods, (for example a combination of NMR or IR and elemental analysis), HCD provides simple mass spectra that are straightforward and easy to interpret.

Electrospray ionization of all of the examined solutions containing analytical mixtures of 2,6-bis(4-methoxybenzoyl)-diaminopyridine (L) and $Cu(NO_3)_2$ (molar ratios: 1:1, 1:4 and 1:10) led to the formation of singly charged ions: $[C_{13}H_{13}O_2N_3+H]^+$ ($m/z_{meas} = 244.1075$, $m/z_{calc} = 244.1086$), $[L+H]^+$ ($C_{21}H_{20}N_3O_4$, $m/z_{meas} = 378.1441$, $m/z_{calc} = 378.1453$), $[CuNO_3^+ + L]^+$ ($C_{21}H_{19}N_4O_7Cu_1$, $m/z_{meas} = 502.0533$, $m/z_{calc} = 502.0549$), $[Cu^{2+} + 2L-H]^+$ ($C_{42}H_{37}N_6O_8Cu_1$, $m/z_{meas} = 816.1959$, $m/z_{calc} = 816.1968$). Ions $[C_{13}H_{13}O_2N_3+H]^+$ were probably formed as a result of small part of L molecules decomposition in the methanol/water solution, or in electrospray ionization process, or during compound storage. Regardless of the origin of the $[C_{13}H_{13}O_2N_3+H]^+$ ions, the most intensive signals on ESI HRMS spectra corresponded to singly charged $[L+H]^+$ ions, which confirms that only a small part of L molecules had been decomposed. Moreover, HRMS spectra showed signals corresponding to complexes formed by L molecules with copper ions (i.e., $[CuNO_3^+ + L]^+$, $[Cu^{2+} + 2L-H]^+$), but did not show signals which could be assigned to complexes formed by $[C_{13}H_{13}O_2N_3+H]^+$ fragments with Cu(II) ions. The ESI HRMS spectrum of the analyzed methanol solution of the mixture of L with metal salt (1:4) is shown in Figure 3. Differences in the molar concentrations of the compound L and copper ions do not affect the type of ions formed but influence the intensity of the signals corresponding to generated products.

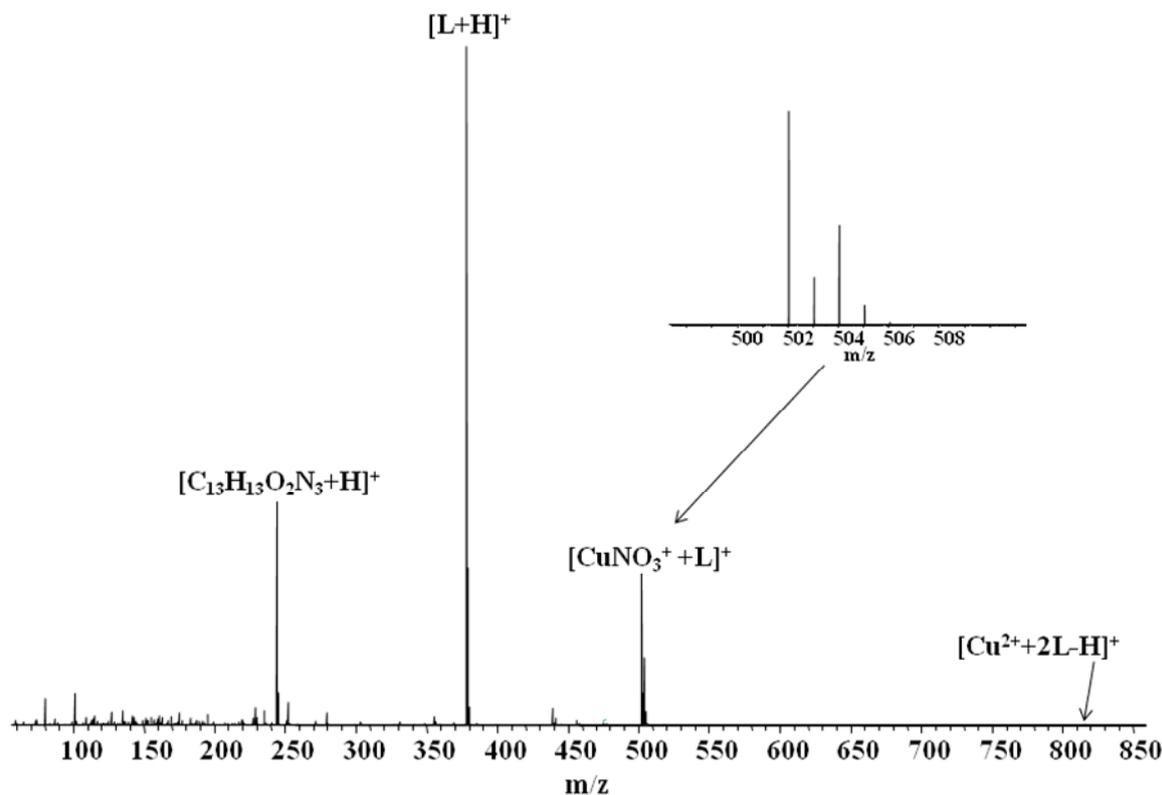
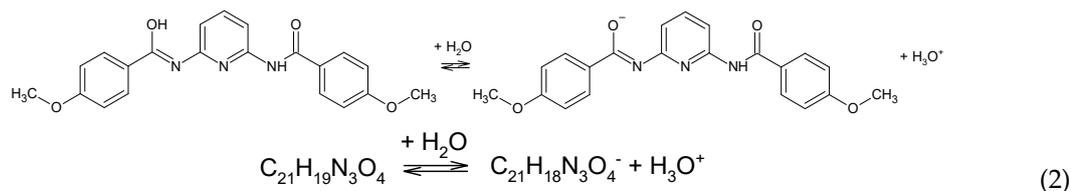


Figure 3. Electrospray ionization (ESI) (+) HRMS mass spectrum of analytical mixtures of L (2,6-bis(4-methoxybenzoyl)-diaminopyridine) and $\text{Cu}(\text{NO}_3)_2$ (molar ratios: 1:4) in methanol. The inset shows the distribution of the isotopic envelope.

Given the high mass accuracy of the HRMS mass spectrometry, there can be no question as to the elemental composition or charge of the ions formed. Based on the results of the performed HRMS experiments, it is possible to conclude that in the process of the formation of copper(II) ions complexes with 2,6-bis(4-methoxybenzoyl)-diaminopyridine can participate both the entire and the deprotonated ligand molecules. It should be emphasized that the HRMS spectrum only shows signals corresponding to ions and the HRMS method does not allow the detection of neutral complexes that can also be formed, e.g., $[\text{Cu}^{2+} + 2\text{L} - 2\text{H}]$. Nevertheless, the results of ESI HRMS experiments clearly confirm that molecules of 2,6-bis(4-methoxybenzoyl)-diaminopyridine (L) are able to form various complexes with Cu(II) ions, but they do not allow to determine all types of possible complexes.

3.2. Dissociation Constant of 2,6-Bis(4-Methoxybenzoyl)-Diaminopyridine

The spectrum of the non-ionized form of the compound is fundamentally different from that of the ionized form. The proposition of dissociation reaction for 2,6-bis(4-methoxybenzoyl)-diaminopyridine is presented by the following equation:



The equilibrium constant pK_a of the above reaction (dissociation constant of the 2,6-bis(4-methoxybenzoyl)-diaminopyridine) is defined as follows:

$$K_a = \frac{[C_{21}H_{18}N_3O_4^-][H_3O^+]}{[C_{21}H_{19}N_3O_4]} \quad (3)$$

From here:

$$- \log K_a = pK_a = pH + \log \frac{[C_{21}H_{19}N_3O_4]}{[C_{21}H_{18}N_3O_4^-]} \quad (4)$$

To determine the characteristic pK_a value of the test compound, the ratio of the concentration of the non-dissociated to dissociated form at the appropriate pH was determined spectrophotometrically. Using the same solution concentrations in subsequent measurements, the formulas for pK_a can be so expressed for acid:

$$pK_a = pH + \log \frac{A_1 - A}{A - A_M} \quad (5)$$

where for the selected wavelength: A_1 —absorbance of the completely ionized form ($C_{21}H_{18}N_3O_4^-$), A_M —absorbance of the non-ionized form ($C_{21}H_{19}N_3O_4$), A —absorbance of a mixture of both forms at a given pH .

For a more precise pK_a determination, several measurements were made at different pH values and the mean value was calculated.

The absorption curve (Figure 4) of the ionized form intersects with the absorption curve of the non-ionized form in the so-called isosbestic point. At this point all the curves of the examined system intersect, regardless of the ratio value $[C_{21}H_{19}N_3O_4]/[C_{21}H_{18}N_3O_4^-]$, because the sum $[C_{21}H_{19}N_3O_4] + [C_{21}H_{18}N_3O_4^-] = C_0$ remains constant which is easy to prove.

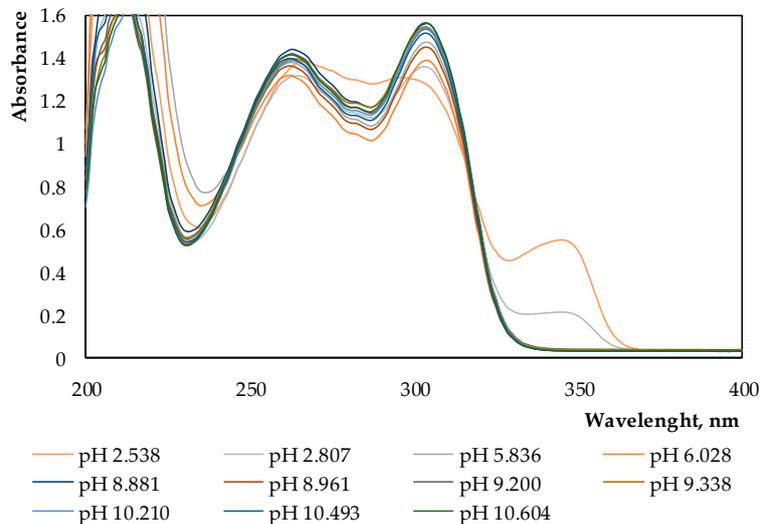
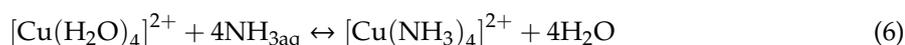


Figure 4. Acid–base balance spectra of 2,6-bis(4-methoxybenzoyl)-diaminopyridine.

The dissociation (pK_a) of investigated ligand determined using the described method was equal to 5.72. The dissociation constant was determined for further adjustment of appropriate conditions to solvent extraction (pH). The obtained value indicated that the best conditions for extraction of metal ions using 2,6-bis(4-methoxybenzoyl)-diaminopyridine were between pH from 5.72 to 7.5. Outside this range, extraction was inhibited for following reasons. First, below the pH value of 5.72 the compound exists only in non-ionized form, which is not able to bind other cations (Equation (2)). Secondly, above pH of 7.5 occurs concurrent reaction a hydrolysis of metal ions. Formation of hydroxides interferes in

the process of recovery metal ions from the solution. Addition of ammonia solution during extraction process prevents creation of metal hydroxides according to reaction:



3.3. Determination of the Stability Constant

The UV spectrum of the complex of copper(II) ions with 2,6-bis(4-methoxybenzoyl)-diaminopyridine is shown in Figure 5. The obtained spectrophotometric spectra are characterized by absorption bands in the UV region between the wavelength 250 and 380 nm.

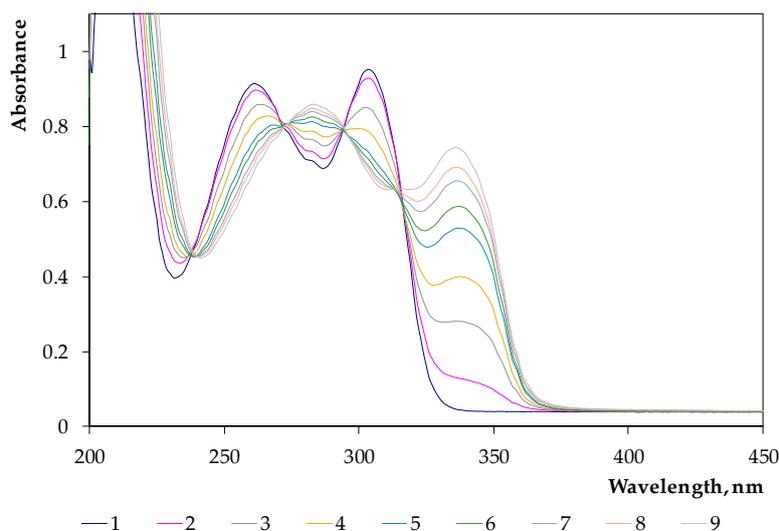


Figure 5. Absorption spectra of Cu(II) complexes with 2,6-bis(4-methoxybenzoyl)-diaminopyridine in various [L] vs. [Cu(II)] molar ratios: 1:0 (1), 1:0.125 (2), 1:0.25 (3), 1:0.375 (4), 1:0.5 (5), 1:0.625 (6), 1:0.75 (7), 1:0.875 (8), 1:1 (9).

Figure 5 shows that Cu/(2,6-bis(4-methoxybenzoyl)-diaminopyridine) complexes were formed in the studied systems. Vanishing of the bands due to ligand $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_4$ (262 nm and 305 nm) and the appearance of new bands (287 nm and 337 nm) together with the isosbestic points at 273 nm and 297 nm were also recorded.

Based on absorption spectra the stability constant (K), was calculated using the Pawlicki et al. [23] method.

The stability constant was determined using Equation (7):

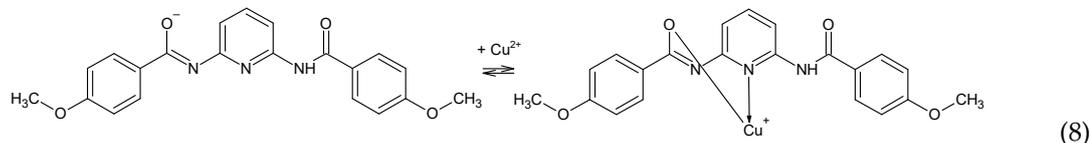
$$\frac{1}{(\varepsilon - \varepsilon_L)} = \frac{1}{K(\varepsilon_C - \varepsilon_L)} \cdot \frac{1}{[\text{Cu(II)}]} + \frac{1}{(\varepsilon_C - \varepsilon_L)} \quad (7)$$

where: $1/(\varepsilon - \varepsilon_L) = y$, $1/[\text{Cu(II)}] = x$, Cu(II) is the molar concentration of Cu(II) ions, mol/dm^3 , $\varepsilon = A/L$, A is the absorbance of the system at 304 nm, L is the molar concentration of the ligand ($\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_4$), mol/dm^3 , ε_L is the molar absorption coefficient of the ligand at 304 nm, and ε_C is the molar absorption coefficient of the complex.

The determined value of the stability constant ($\log K$) of Cu(II)/(2,6-bis(4-methoxybenzoyl)-diaminopyridine) complex, in which molar ratio L vs. Cu(II) is 1:1, were equal to 5.5 ± 0.1 .

3.4. Solvent Extraction

One of the possible, most likely coordination processes of coordination copper ions to investigated ligand during extraction is presented using the following Equation (8):



It is well known that Schiff bases can be created by ketones and amines [24]. The Schiff bases can create a metal complexes with transition metals [25].

In the case where there is no phase change in volume, distribution ratio of metal ion ($D_{\text{Cu(II)}}$) was defined as follows:

$$D_{\text{Cu(II)}} = \frac{C_{\text{Cu(II)}}(\text{org})}{C_{\text{Cu(II)}}(\text{aq})} = \frac{C_{\text{Cu(II)}}^0 - C_{\text{Cu(II)}}}{C_{\text{Cu(II)}}} \quad (9)$$

where: $C_{\text{Cu(II)}}^0$ and $C_{\text{Cu(II)}}$ denote analytical copper ions concentrations in the aqueous phase before and after extraction, respectively.

Based on analytical calculations for each equilibrium value of pH for the aqueous phase, the distribution ratios ($D_{\text{Cu(II)}}$) were calculated using Formula (9) and subsequently extraction curves (Figure 6) were plotted for investigated ligand ($\log D_{\text{Cu(II)}} = f(\text{pH})$).

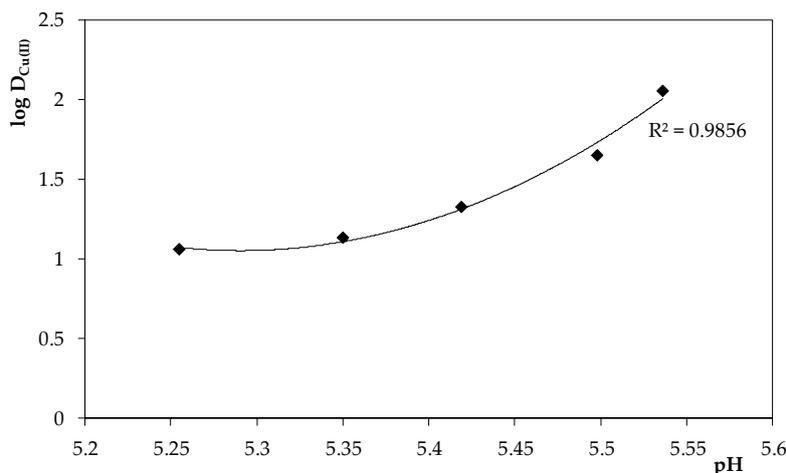


Figure 6. Relation $\log D_{\text{Cu(II)}} = f(\text{pH})$ in process of extraction Cu/(2,6-bis(4-methoxybenzoyl)-diaminopyridine) complexes.

The $\log D_{\text{Cu(II)}}$ coefficient increases with ligand concentration increasing.

The percentage of copper(II) ions extraction was calculated using the following formula:

$$\%E_{\text{Cu(II)}} = \frac{D_{\text{Cu(II)}} \cdot 100\%}{D_{\text{Cu(II)}} + V_{\text{aq}}/V_{\text{org}}} \quad (10)$$

where: V_{aq} and V_{org} —volumes of aqueous and organic phases.

Table 1 shows dependence between the percentage of copper(II) ions extraction and concentration of ligand in the organic phase.

The highest percentage extraction of copper (99.13%) at pH 5.53 was obtained for 0.001 mol/dm³ concentration of ligand in organic phase, whereas the lowest $\%E_{\text{Cu(II)}}$ was observed for 0.0001 mol/dm³ concentration. The obtained results of solvent extraction indicated that the studied compound could be used as extractant.

Table 1. Relation between ligand concentration in organic phase and percentage of copper(II) ions extraction.

Concentration of the Ligand in Organic Phase, mol/dm ³	%E _{Cu(II)}
0.00010	91.98
0.00025	93.16
0.00050	95.49
0.00075	97.83
0.00100	99.13

The given values of the %E_{Cu(II)} carry 0.7% tolerance.

4. Conclusions

Obtained in this work, results indicated that the new compound 2,6-bis(4-methoxybenzoyl)-diaminopyridine could be used as extractant in solvent extraction. During the studies, more than 99% of copper(II) ions were extracted from 0.001 mol/dm³ Cu²⁺ water solution (pH~5.8) using chloroform phase, which contained 0.001 mol/dm³ 2,6-bis(4-methoxybenzoyl)-diaminopyridine. The electrospray ionization high-resolution mass spectrometry (ESI HRMS) and the higher energy collisional dissociation tandem mass spectrometry (HCD MS/MS) methods have been successfully used to confirm the structure of 2,6-bis(4-methoxybenzoyl)-diaminopyridine and its ability to form complexes with Cu²⁺ ions in solution. The fairly high stability of the created complexes with 2,6-bis(4-methoxybenzoyl)-diaminopyridine and Cu²⁺ ions was proved in spectrophotometry tests.

The obtained results indicate that in future 2,6-bis(4-methoxybenzoyl)-diaminopyridine can be used in other processes for metal ions recovery, for example, as an ion carrier in polymer inclusion membrane.

Author Contributions: The synthesis of 2,6-bis(4-methoxybenzoyl)-diaminopyridine was done by B.O., the solvent extraction process was conducted by D.B., K.W. determined the dissociation constant of 2,6-bis(4-methoxybenzoyl)-diaminopyridine and stability constant of its complex with copper(II) ions, M.A.K. planned all of the HRMS and HCD MS/MS experiments and analyzed the obtained mass spectra.

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Conflicts of Interest: The authors declare no conflict of interest.

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