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A NOVEL N-PIVOT MACROCYCLIC LIGAND AND ITS COBALT(II) PHTHALOCYANINE DERIVATIVE: SYNTHESIS, CHARACTERIZATION AND EXTRACTANT PROPERTIES

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ABSTRACT

In this study, the synthesis of a novel N-pivot 12-membered macrocyclic ligand with mixed donor atoms ***2****, which is a phthalonitrile derivative, and a new cobalt(II) phthalocyanine complex* ***3*** *obtained by cyclotetramerization reaction of* ***2*** *were described. Newly synthesized compounds were characterized by using several spectroscopic techniques such as IR, UV-Vis,* ^{1}*H and* ^{13}*C NMR, MS and elemental analysis. These macrocyclic systems* ***2*** *and* ***3*** *were investigated as extractants in liquid-liquid extraction technique to reveal metal ion binding capability towards transition metals such as Ag(I), Hg(II), Cd(II), Zn(II), Cu(II), Ni(II), Pb(II) and Co(II). The highest extractability from aqueous phase to organic phase was found for Hg(II) cation over the other metal cations with cobalt(II) phthalocyanine* ***3****. The extraction percentage of Hg(II) cation from aqueous phase to chloroform in the presence of cobalt(II) phthalocyanine* ***3*** *as extractant was found as 96.0%.*

1. INTRODUCTION

First synthesis of macrocycles was reported by Pedersen in 1967 [1]. Since then, hundreds of macrocycles have been synthesized [2] and applied in most of research areas, such as removing heavy metals from aqueous solution [3], recognition of anions/cations, receptor for neutral molecules, due to their unique architecture, stabilities and functions [4]. Various types of macrocycles including a variety of type of donor atoms such as oxygen, sulfur, nitrogen and phosphorus have been studied for understanding of metal-ion binding properties of macrocycles [5]. These studies showed that designing of a macrocyclic ligand with appropriate size and donor atoms is the key step to achieve a selective complexation of metal ion. The hard-soft acid-base concept is the preliminary guide for selection of donor atom type. According to this concept, macrocycles with soft donor atoms such as sulfur prefer to bind soft transition metal ions whereas hard oxygen containing macrocyclic ligands show a binding preference toward alkali metal cation.

In 1934, the synthesis of phthalocyanines by the reaction of o-cyanobenzamide with cupper(I) cyanide at high temperature were reported by Linstead [6]. They have been mostly used as green and blue dyes since their first synthesis. Nowadays, these compounds have attracted great attention due to the potential applications in cancer therapy as photodynamic reagent [7], solar cells as dye material [8], catalysis as catalyst and computer science as optical materials. Incorporation of macrocycles into a phthalocyanine skeleton was presented as first in 1986 by Bekaroğlu and co-workers [9]. Later on, the complexation properties of this new molecule, phthalocyanine-bearing macrocycle, were reported by Musluoğlu [10]. Until now, many numbers of phthalocyanines bearing macrocycle with different ring size and type of donor atoms at peripheral or non-peripheral positions have been synthesized [11] and found potential application in removing metal ion from aqueous media [12].

In our previous work, we have reported the synthesis of metal-free and metallophthalocyanines bearing macrocycles with different ring size and mixed donor atoms, and investigation of their metal-ion binding properties towards transition metals [12]. As part of going interest toward investigation of complexation behavior of phthalocyanine bearing macrocycle, herein, we wish to report the synthesis, characterization and

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extractant properties of a novel 12-membered macrocycle with mixed donor atoms and its cobalt(II) phthalocyanine derivative.

2. METHODS

The extractant properties of newly synthesized compounds **2** and **3** towards transition metal ions such as Ag(I), Hg(II), Cd(II), Zn(II), Cu(II), Ni(II), Pb(II), and Co(II) were investigated by the method of solvent extraction based on non-mixing biphasic liquid-liquid system. The experiments were performed by following the well-established literature procedure [13-15]. For liquid-liquid solvent extraction, the metal picrate solutions were prepared by mixing of metal nitrates and picric acid in distilled water. Chloroform was chosen as an organic solvent. 10 mL of chloroform containing 1.25 x 10^{-4} M ligand and 10 mL of metal picrate solutions (picric acid, 1.25 x 10^{-5} M; metal nitrate, 1 x 10^{-2} M) was placed together in stoppered flask and then shaken for 2 h at 20 ± 0.1 °C followed by standing for at least 2 h at the same temperature in order to complete the phase separation. The aqueous phase was measured at 355 nm by UV-Vis spectrophotometer to determine the remaining picrate ion concentration. By following the same experiment procedure in the absence of macrocycles **2** and **3**, the blank experiments were also performed and no picrate extraction was determined at the measurements.

The extraction percentage (E%) of each metal cation was calculated by using the following equation [16, 17]:

$$E(\%) = \frac{[A_0 - A]}{A_0} x100 \qquad (1)$$

A_0: the absorbance of the tested transition metal picrate in the absence of ligand

A: the absorbance of the tested transition metal picrate in the aqueous phase after extraction

During the solvent extraction process, the general extraction equilibrium can be proposed as:

$$M^{n+}_{aq} + nPic^{-}_{aq} + mL_{org} \Leftrightarrow [M(Pic)_n(L)_m]_{org} \qquad (2)$$

If the Eq.(2) is reorganized by using distrubition ratio *D* and extraction equilibrium constant *K* as below, the plot of log {D/[Pic$^-$]^n} as a function of log [L] should give a straight line with a slope of *m* and log K$_{ex}$ can be calculated from the intercept by using Eq.(3), which is valid for the extraction system [13-15]. For these studies, we used the macrocycles concentration in the range of 2.5 x 10^{-6} to 7.5 x 10^{-5} M.

$$\log\left(\frac{D}{[Pic^-]^n}\right) = \log K_{ex} + m\log[L] \qquad (3)$$

3. EXPERIMENTAL

3.1. Materials and Equipment

Starting precursor named as N,N'-(2,2'-(4,5-dicyano-1,2-phenylene)bis(sulfanediyl)bis(2,1-phenylene))bis(2-chloroacet-amide) **1** was prepared by following the published procedure [18]. All reagents and solvents were reagent grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [19].

FTIR spectra were measured on a Perkin Elmer Spectrum 65 spectrometer in KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer in CDCl$_3$. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS and a Bruker Daltonics MALDI-TOF spectrometer. Optical spectra were recorded in the UV-Vis region with a PG-T80+ spectrophotometer in 1 cm path length cuvettes at room temperature. The elemental analyses were obtained with a LECO Elemental Analyzer (CHNS 0932) spectrophotometer. The melting points were determined with an electrothermal apparatus and are reported without correction. In solvent extraction experiment Selecta type shaker with thermostat was used.

3.2. Synthesis

3.2.1. 10-(2-chloroacetyl)-12-oxo-10,11,12,13-tetrahydrotribenzo[b,e,k][1,4]dithia[7,10]diazacyclododecine-2,3-dicarbonitrile (2)

Compound **1** (1.0 g, 1.9 mmol) was added to a solution of 10 mL THF containing KOH (0.16 g, 2.85 mmol) as the base. The resulting reaction mixture was cooled to 0 °C and stirred for 10 h under nitrogen atmosphere. Reaction progress was followed by TLC using a solvent mixture of ethyl acetate-hexane (4:6). When the reaction was completed, 20 mL of water and 50 mL of dichloromethane were added to the reaction mixture and stirred for further 20 min at room temperature. Dichloromethane phase was separated and washed with 5% NaCl solution (15 mL) and water (2 x15 mL), respectively. Later, the combined organic layer was separated and anhydrous Na_2SO_4 was added to remove trace of water from the organic phase. Then, the Na_2SO_4 in dichloromethane was separated by filtration. Removing the solvent under reduced pressure afforded the crude product which was purified by silica gel chromatography. The elution was carried out with hexane-ethyl acetate (7:3). The product was obtained as pale yellow solid and then dried in vacuum. The yield was 0.5 g (52%). mp 185-187 ^{o}C. Anal. calcd for $C_{24}H_{15}ClN_4O_2S_2$: C, 58.71; H, 3.08; N, 11.41; S, 13.06%. Found: C, 58.52; H, 3.34; N, 10.93; S, 12.22%. IR (KBr disc) ν_{max}/cm^{-1}: 3322(NH), 3092, 3062 (CH$_{Ar}$), 2924 (CH$_3$), 2232 (C≡N), 1689 (C=O), 1580, 1519, 1476, 1436, 1298, 1258, 1129, 1037, 755, 663, 527. ^{1}H NMR (CDCl$_3$) δ: 8.86 (s, H, NH), 8.59 (d, H, ArH), 7.63 (s, H, ArH), 7.62 (t, H, ArH), 7.54 (t, H, ArH), 7.51 (d, H, ArH), 7.27 (t, H, ArH), 7.19-7.13 (m, 2H, ArH), 7.02 (s, H, ArH), 6.46 (m, H, ArH), 4.16 (H$_a$, J_{AB}=14,5 Hz), 4.13 (H$_b$, J_{AB}=14,5 Hz), 3.66 (H$_c$, J_{CD}=14,5 Hz), 3.65 (H$_d$, J_{CD}=14,5 Hz). ^{13}C NMR (CDCl$_3$) δ:

164.67, 164.51, 146.27, 140.05, 140.01, 138.37, 137.65, 134.81, 133.43, 131.11, 129.06, 127.77, 126.04, 125.23, 123.97, 121.92, 118.78, 116.61, 114.52, 114.39, 114.31, 113.68, 43.29, 31.81. MS (LC-MS/MS) m/z: 491.27 $[M+H]^+$, 513.17 $[M+Na]^+$,

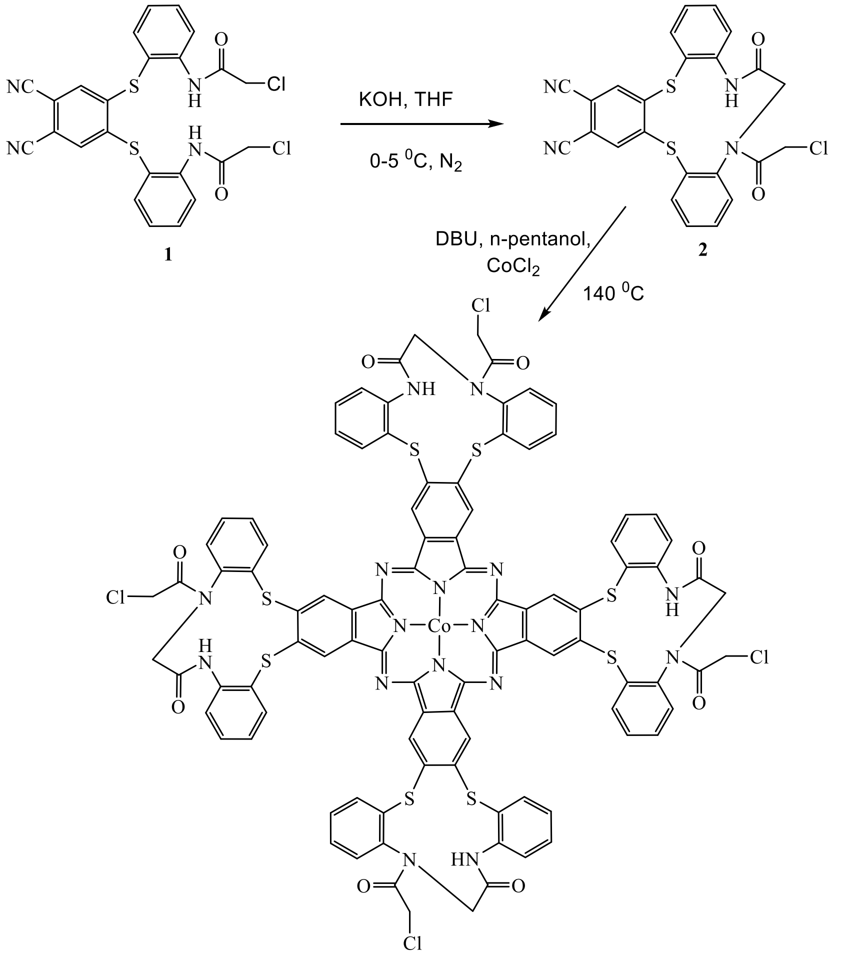
3.2.1. Cobalt(II) phthalocyanine (3)

The cyclotetramerization reaction of 10-(2-chloroacetyl)-12-oxo-10,11,12,13-tetrahydrotribenzo[b,e,k][1,4]dithia[7,10]diazacyclododecine-2,3-dicarbonitrile **2** (0.15g; 0.30 mmol) in the presence of anhydrous $Co(CH_3CO_2)_2$ (0.016g; 0.092 mmol) and 2 mL of quinolone was accomplished in a Schlenk tube under nitrogen atmosphere at 190 °C for 7 h. At the end of this period, the reaction mixture was cooled to room temperature and 10 mL of ethanol was added to this stirring reaction mixture. The precipitate was filtered off and washed several times with ethanol. The crude product was further purified by refluxing with ethanol in a Soxhlet extractor for 4h. The product was then filtered and washed with ethanol and diethyl ether and then dried under vacuum. The yield was 0.040g (21%). mp: >300 °C. Anal. calcd for $C_{96}H_{60}Cl_4CoN_{16}O_8S_8$: C, 57.00; H, 2.99; N, 11.08%. Found: C, 56.52; H, 3.18; N, 10.87%. IR (KBr disc) ν_{max}/cm^{-1}: 3359 (-NH), 3061, 2923, 1683 (C=O), 1583, 1507, 1476, 1441, 1335, 1294, 1259, 1079, 751. UV-Vis (DMF): λ_{max}, nm (log ε): 352 (4.73), 476 (4.01), 690 (4.69); MALDI-TOF (ESI^+) (*m/z*): calculated $[M+4H_2O]^+$ for $C_{96}H_{68}Cl_4CoN_{16}O_{12}S_8$: 2094.1 found: 2093.9.

4. RESULTS AND DISCUSSION

4.1. Synthesis and Characterization

The synthetic pathway for preparation of N-pivot 12-membered macrocyclic ligand **2** and cobalt(II) phthalocyanine **3** is summarized in Scheme 1. The structures of novel compounds were characterized by a combination of elemental analysis and ^1H NMR, ^{13}C NMR, IR, UV-vis and MS spectral data.



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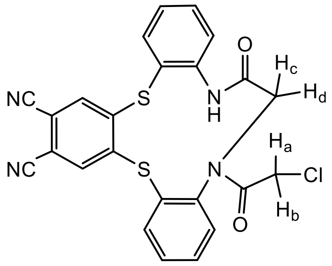
Scheme 1. *Synthetic route of macrocyclic ligand **2** and its cobalt(II) phthalocyanine derivative **3***

Reaction of N,N'-(2,2'-(4,5-dicyano-1,2-phenylene)bis(sulfanediyl)bis(2,1-phenylene))bis(2-chloroacet-amide) **1** and KOH in THF at 0 ^{0}C under nitrogen atmosphere afforded 10-(2-chloroacetyl)-12-oxo-10,11,12,13-tetrahydrotribenzo[b,e,k][1,4]dithia[7,10]diazacyclododecine-2,3-dicarbonitrile **2** in 52% yield after purification by column chromatography using hexane-ethyl acetate

(7:3) as solvent system. The formation of 12 membered N_2S_2 mixed donor macrocyclic compound was occurred by self condensation reaction one of two N-substituted 2-chloroamides of **1**. The cyclization reaction was confirmed by the appearance of the specific stretching vibration of the –NH groups 3322 cm^{-1} in the IR spectrum of **2**. The intense vibrations at 2232 cm^{-1} and 1689 cm^{-1} was attributed to the C≡N and C=O groups in the structure of **2**, respectively. In the ^{1}H NMR spectrum of **2**, the singlet for -NH proton in the amide moiety was observed at δ = 8.86 ppm as expected. Protons of the nitrile substituted benzene ring were appeared as two singlets at δ = 7.63 and 7.02 ppm. Macrocycle **2** has four diastereotopic protons due to its asymmetric structure. These diastereotopic protons were shown in Scheme 2 and were appeared as AB spin system at δ = 4.16, 4.13 and 3.66, 3.64 ppm with a coupling constant of J = 14.5 Hz.



(2)

Scheme 2. *Diastereotopic protons (H_a, H_b, H_c, H_d) of macrocyclic ligand **2***

The ^{13}C NMR spectrum of **2** indicated the presence of carbonil and methylene carbons at δ = 164.57, 164.51 and 43.29, 31.81 ppm, respectively. The mass spectrum of macrocycle **2** was obtained by LC-MS/MS technique and the expected molecular ion peak for **2** was observed at m/z = 491.27 $[M+H]^+$ and 513.17 $[M+Na]^+$.

The cyclotetramerization of the phthalonitrile derivative **2** in the presence of cobalt(II) acetate to the cobalt(II) phthalocyanine **3** was accomplished in quinoline at 190 °C for 7 h under nitrogen in a Schlenk tube to afford **3** in 21% as green amorphous solids after purification by soxhlet extraction. After conversion of the dinitrile precursors containing macrocycle **2** to the phthalocyanines, the sharp C≡N vibration around 2232 cm^{-1} disappeared in the IR spectra of phthalocyanine derivatives. IR spectra of cobalt(II) phthalocyanine **3** is very similar to the IR spectra of **2** and indicated the aromatic groups at around 3060 cm^{-1}, the aliphatic groups at around 2900 cm^{-1} and the C=O group at around 1683 cm^{-1} by intense bands. A close investigation of the mass spectra of the cobalt(II) phthalocyanine **3** confirmed the proposed structure. Acquired MALDI-TOF spectra of phthalocyanine derivative **3** has allowed us to record molecular ion peaks at m/z = 2093.9 $[M+4H_2O]^+$, confirmed the proposed structure. In addition to the mass spectra, the electronic absorption spectrum of the studied phthalocyanine was recorded in DMF. Phthalocyanine complex showed the expected absorptions with the main peaks of the Q and B bands, appearing a band at λ_{max} = 690 nm and 352 nm, respectively. Appearance of single intense Q band is characteristic for metallophthalocyanines with D_{4h} symmetry [20].

4.2. Extractability

The metal ion-binding properties of macrocycle **2** and cobalt(II) phthalocyanine **3** was performed by using solvent extraction experiments in order to estimate the extractability of metal ions such as Ag^+, Hg^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Co^{2+} from aqueous phase to the organic phase. Chloroform was used as an organic solvent to reveal extraction efficiency. The results related to the extractability of above metal picrates from aqueous phase to organic phase are given in Table 1.

Table 1. *The extractability of aqueous metal picrates for **2** and **3** into chloroform phase*

Compound*	**Extractability (%)**							
	Ni^{2+}	Cu^{2+}	Hg^{2+}	Zn^{2+}	Ag^+	Cd^{2+}	Pb^{2+}	Co^{2+}
(2)	<1	<1	6.8±0.4	<1	5.8±0.4	<1	<1	<1
(3)	67.0±1.2	92.2±2.1	96.0±1.1	41.7±2.3	92.7±0.8	77.0±1.2	92.1±1.9	62.6± 0.3

**Temperature: 20.0±0.1 °C; aqueous phase (10 mL); $[pic^-] = 1.25 \times 10^{-5}$ M, organic phase (10 mL); $[L] = 1.25 \times 10^{-4}$ M; The values calculated from three independent extraction experiments.*

As seen from Table 1, macrocyclic ligand **2** exhibited the lowest extraction efficiency for all the metal ions in both solvents. The best extractability belongs to Hg^{2+} ion and Ag^+ ion in chloroform, but they were only 6.8% and 5.8%, respectively. The cation binding properties of the macrocycles depend upon different factors such as macrocylic effect, cavity size, and the type and number of donor atoms [4, 5]. As seen from Scheme 1, the cobalt(II) phthalocyanine **3** contains four macrocycle unit and it is expected to transport metal cations more effectively with respect to macrocycle **2** for the same conditions. In addition to that, the cobalt (II) phthalocyanine **3** has a planar structure. The E% values obtained for cobalt(II) phthalocyanine **3** was higher than those of macrocycle **2** in chloroform. The obtained extraction values in the presence of cobalt(II) phthalocyanine **3** for Ag^+, Hg^{2+}, Pb^{2+} and Cu^{2+} in chloroform were high when compared to other metal cations. The highest extractability belongs to Hg^{2+} and Ag^+ cations with cobalt(II) phthalocyanine **3** . The values of extractability belonging to Hg^{2+} and Ag^+ are 96.0% and 92.7% in chloroform, respectively. In the case of cobalt(II) phthalocyanine **3**, increasing in extraction capability may be due to the result of planarity of cobalt(II) phthalocyanine **3** or the number of donor atoms in compound **3**. From the experimental results, we can conclude that the cobalt(II) phthalocyanine **3** is much more effective than macrocyclic ligand **2** in the extractability of metal cations from aqueous phase to organic phase under these conditions.

To determine complex composition (M:L) between cobalt(II) phthalocyanine **3** and the most extracted two metal cations which are Hg^{2+} and Ag^{+}, and extraction constant log K_{ex} of those extracted complex species, the distribution ratio D of the cation between the aqueous phase and the organic phase upon concentration of cobalt(II) phthalocyanine **3** was examined. Fig. 1 and Table 2 showed the obtained results from these experiments. As shown from the results, the liquid-liquid extraction experiments with different metal cations such as Hg^{2+} and Ag^{+} in the presence of cobalt(II) phthalocyanine **3** resulted in same complex compositions. Hg^{2+} and Ag^{+} metal ions gave 3:2 complex composition with cobalt(II) phthalocyanine **3** for chloroform. The log K_{ex} values for 3:2 complex composition between Hg^{2+} and Ag^{+}, and cobalt(II) phthalocyanine **3** were 12.5 and 11.5, respectively.

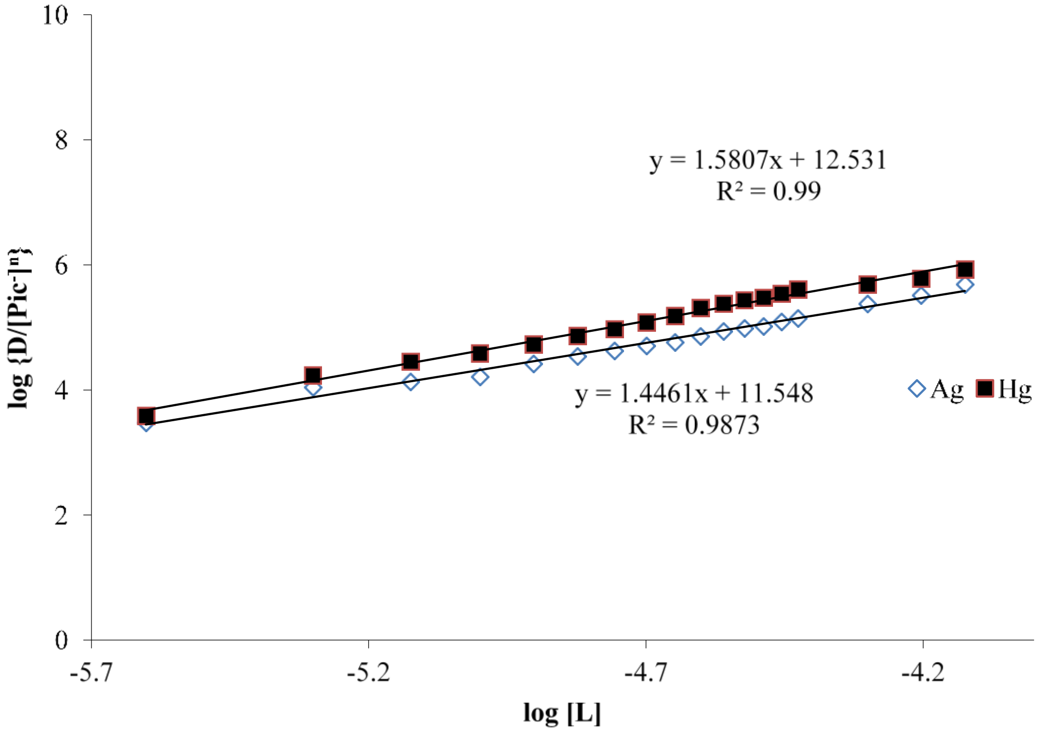


Figure 1. *log {D/[Pic⁻]ⁿ} versus log [L] for the extraction of Ag(I) and Hg(II) -picrate with cobalt(II) phthalocyanine **3**, solvent:chloroform*

Table 2. *The relationship between composition and extraction constant for cobalt(II) phthalocyanine **3**-Ag(I) and Hg(II) complexes in chloroform phase*

Cation	Extraction constant ($logK_{ex}$)	m (the slope)	Complex composition (L:M)
Ag(I)	11.5 ± 0.4	1.4 ± 0.1	3:2
Hg(II)	12.5 ± 0.3	1.6 ± 0.1	3:2

5. CONCLUSIONS

We described the synthesis of a new N-pivot 12-membered macrocyclic ligand with diazadithia donor atoms and its cobalt(II) phthalocyanine derivative. The characterization of newly synthesized compounds **2** and **3** was performed by a combination of FT-IR, UV-Vis, ^{1}H and ^{13}C NMR, MS and elemental analysis measurements. After that, solvent extraction method was carried out to reveal the metal-ion binding properties of macrocyles **2** and **3.** UV-Vis measurements to determine the remaining picrate ion concentration in the aqueous phase following the liquid-liquid extraction experiment showed that cobalt(II) phthalocyanine complex **3** has higher cation binding capacity that macrocycle **2.** The highest extraction value was obtained for Hg^{2+} among the other cations with cobalt(II) phthalocyanine **3.** The extraction percentage of Hg^{2+} with **3** from aqueous phase to chloroform was found as 96.0%. Furthermore, obtaining a very high extraction constant log K_{ex} value such as 12.5 between Hg^{2+} cation and cobalt(II) phthalocyanine **3** proved the stability of the formed complex. As a result, cobalt(II) phthalocyanine have the potential to be used in extraction of Hg^{2+} ion from industrial wastewaters successfully.

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