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Solvent Extraction of Ag(I) and Cu(II) with New Macrocyclic Schiff Bases

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Two new macrocyclic Schiff bases (II) and (III) containing nitrogen - oxygen donor atoms were synthesized by reaction between diethylene triamine or 2,2'-(ethylenedioxy)bis(ethylamine) and the intermediate compound: 1,4-bis(6-methoxy-2-formylphenyl)-1,4-dioxabutane (I). Identification of these macrocyclic Schiff bases: 1,12, 15,18, 29,32 - hexaaza - [3,4;8,9;20,21;26,27-tetra-(6'-methoxyphenyl)]-5,8,22,25-tetraoxa cyclo tetratriacosine-1,11,18,28-tetraene. (II) 1,12,21,32-tetraaza-[3,4;9,10;23,24;29, 30-tetra-(6'-methoxyphenyl)]-5,8,15,18,25,28,35,38-octaoxa cyclo - tetracontane-1,11,21,31-tetraene. (III) were determined by elemental analysis (LC-MS), (IR) and (¹H and ¹³C-NMR) spectroscopy. The liquid-liquid extraction of metal picrates such as Ag⁺ and Cu²⁺ from aqueous phase to organic phase was carried out using these ligands. The effect of chloroform and dichloromethane as organic solvents over the metal picrate extractions were investigated at 25 ± 0.1 °C by using atomic absorption spectrometer.

Keywords: Macrocyclic Schiff bases; Liquid-liquid extraction.

INTRODUCTION

Polyaza macrocycles with large cavities have received recent interests as inorganic cation receptors. The cyclic arrangement of a large number of donor atoms and the flexibility of these ligands make them good hosts for ion complexes.^{1,2} They were also used as spectrophotometric analytical reagents. Metal ions have enormous importance in many biological processes, especially heavy metal ions are effective enzyme inhibitors exerting toxic effects on living system.³ Therefore, separation and determination of toxic metal ions such as mercury, lead, and cadmium in environmental sources play an important role for healthy life. Although new macrocyclic compounds containing oxygen, sulfur, and nitrogen are knowing. Macrocyclic compounds used in solvent extraction were mostly the oxygen donar type.⁴ A number of methods for the preparation of the large polyaza macrocyclic have been reported. The most common synthetic procedure requires the use of N-tosyl groups to protect and activate the nitrogen atoms in the cyclization step.⁵ Ring closure occurs by a condensation reaction of N-tosylated polyamines with the appropriate ditosylate ester or dihalide in DMF in the presence of base.⁶ These reactions allow the production of polyaza macrocycles in moderate yields, but removing the N-tosyl groups requires drastic conditions and is not always straightforward.⁷ Another cyclization process uses the template ring closure for formation of cyclic di- or tetra dental Schiff base. This is a simple process, but it is often difficult to

choose the correct template metal ion or to predict certain ring contraction reactions were the template cation dose not coordinate with all of the ring nitrogen atoms.⁸ In some cases, reduction of the cyclic Schiff base and removal of the template ion have been difficult.⁹ A non template method for the formation of macrocyclic poly Schiff bases has also been studied. This procedure often gave a polymeric material beside cyclization reaction, while there is no need to remove a metal ion.¹⁰ In the present work we used a non template method for the formation of two novel macrocyclic Schiff bases having ethoxy groups: (II) and (III) Scheme I, then were used for removel of various metal ions from the aqueous phase in to the organic phase in liquidliquid extraction system.

EXPERIMENTAL

Materials and method

Chloroform, dichloromethane, dimethyl formamide, picric acid, methanol, K₂CO₃, Cu(NO₃)₂.3H₂O, Ag(NO₃), were the analytical grade reagents and were purchased from Merck. Diethylene triamine, 2,2'-(ethylenedioxy)bis-(ethylamine), 1,2-dibromoethane and o-vanillin were record from sigma-Aldrich. IR spectra was obtained on Jusco 300 FT-IR Spectrometer using KBr discs. Mass spectra of the ligand were carried out on a micro mass Quattro LC-MS/MS Spectrometer. ¹H-NMR and ¹³C-NMR spectra was recorded at ambient Broker DT-400 Spectrometer using CDCl₃ with DMSO-DMF as the internal standard. A Hita-

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Article



Scheme I Structure of the macrocyclic Schiff bases (II), and (III)

chi Model 180-80 Atomic absorption Spectrometer (acetylene/air flame) was used to determine the concentration of metal ions.

Synthesis of 1,4-bis(6-methoxy-2-formylphenyl)-1,4dioxabutane (I)

To a stirred solution of o-vanillin (3.04 g, 0.02 mol) and K₂CO₃ (1.38 g, 0.01 mol) in DMF (50 mL) 1,2-dibromoethane (1.88 g, 0.01 mol) in DMF (10 mL) was added dropwise the reaction was continued for 10 h at 150-155 °C and then 5 h at room temperature after the addition was completed, 20 mL distilled water was added it was left in refrigerator for 1 h later the precipitate was filtered, washed by 50 mL water, dried in air, re-crystallized from ethanol.¹¹ Colour: bright brown. m.p: 180-182 °C. Yield: (4.6, 70%), Mass spectra: m/z = 330; IR (KBr pellets, cm⁻¹): 3003 (aromatic-CH), 2930-2887 (Aliphatic-C-H), 1700 (C=O)_{str}, 1482-1475 (aromatic C=C), 1289, 1311 (Ar-O), 1181 (O-CH₃), 1130, 1100 (R-O), 757 (substituted benzene).

Synthesis of 1,12,15,18,29,32-hexaaza-[3,4;8,9;20,21; 26,27-tetra-(6'-methoxyphenyl)]-5,8,22,25-tetraoxa-cyclotetratriacosine-1,11,18,28-tetraene (II)

The macrocyclic compound (II) was prepared by the dropwise addition of solution of the diethylene triamine (0.206 g, 2 mmol) in methanol (40 mL) to a stirred solution of compound (I) (0.66 g, 2 mmol) in methanol (60 mL), the stirring was continued for 10 h, an oily product began to separate from solution. It was purified by washing with ethanol. The large macrocyclic product pal yellow oil. Yield: (1.0 g, 64%); Mass spectra: $m/z = 795 [II+H]^+$. IR (KBr pellets, cm⁻¹): 3200 (–N-H), 3080 (aromatic–CH), 2920-2847 (Aliphatic -C-H), 1640 (CH=N)_{str}, 1488-1460 (aromatic

C=C), 1287, 1238 (aromatic-O), 1220 (O-CH₃), 1180, 1130 (R-O), 756 (substituted benzene). ¹H and ¹³C-NMR spectra in CDCl₃are complex. ¹²

¹H-NMR (CDCl₃-d₆): 8.78 (s, 4H, CH=N), 6.74-7.62 (m, 24H, Ar–H), 4.72 (t, 4H, -CH₂-NH-), 3.90, 3.97 (t, 4H, CH₂-O-ph), 3.70, 3.77, 3.78, 3.80 (t, 4H, CH₂-O-), 2.29, 2.26 (s, 12H, O-CH₃), ¹³C-NMR (CDCl₃-d₆, δ ppm): OCH₃: 56.72, 57.03, 57.95, NH-CH₂: 69.65, 67.71, OCH₂: 73.03, 73.72. Aromatic: 111.99, 112.53, 116.25, 117.95, 119.41, 120.91, 122.26, 122.08 128.32, 143.01, 144.14, 156.65, 159.97, HC=N: 169.93, 167.51. Anal. Calc. For C₄₄H₅₄N₆O₈: C, 66.5; H, 6.8; N, 10.6. Found: C, 66.4; H, 6.9; N, 10.9; $[\alpha]_D^{20.5} = 1.62$.

Synthesis of 1,12,21,32-tetraaza-[3,4;9,10;23,24;29,30-tetra-(6'-methoxyphenyl)]-5,8,15,18,25,28,35,38-octaoxacyclo-tetracontane-1,11,21,31-tetraene (III)

The macrocyclic compound (III) was prepare by the dropwise addition of solution of the 2,2'-(ethylenedioxy) bis(ethylamine) (0.74 g, 5 mmol) in methanol (60 mL) to a stirred solution of compound (I) (1.66 g, 5 mmol) in methanol (60 mL). After the addition was completed, the stirring was continued for 10 h, an oily product began to separate from solution. It was purified by washing with ethanol, the large macrocyclic product pal yellow oil. Yield: (2.6 g, 60%), Mass spectra: m/z = 882 [III-2H]⁺. IR (KBr pellets, cm⁻¹): 3026 (aromatic–CH), 2888-2847 (Aliphatic-C-H), 1650 (CH=N). 1488-1460 (aromatic C=C), 1287, 1238 (aromatic-O), 1222 (O-CH₃), 1180, 1130 (R-O), 754 (substituted benzene). ¹H and ¹³C-NMR) spectra in CDCl₃ are complex.¹² ¹H-NMR (CDCl₃-d₆): 8.52 (s, 4H, CH=N), 7.10-7.74 (m, 12H, Ar-H), 4.31-4.5 (t, 8H, O-CH₂-CH₂), 3.97 (t, 4H, O-CH₂-), 3.89 (t, 4H, CH₂-O-ph), 2.41 (s, 12H, O-CH₃). ¹³C-NMR (CDCl₃-d₆, δ ppm): OCH₃: 40.15, CH₂-O-Ph: 69.35, 69.03, 66.72, OCH₂: 70.32, 71.91, 72.54, 73.26, 74.97, 75.49, Aromatic: 102.91, 111.08, 122.26, 122.32, 124.01, 134.14, 136.65, 139.97, 149.51, 150.93, HC=N: 166.15, 167.27. Anal. Calc. For C₄₈H₆₀N₄O₁₂: C, 65.1; H, 6.8; N, 6.3; Found: C, 65.4; H, 7.1; N, 6.0; $[\alpha]_D^{20.5}$ = 1.88.

Solvent extraction

Transition metal picrates were prepared by the stepwise addition of a 1×10^{-2} M of metal nitrate solution to a 1.25×10^{-4} M aqueous picric acid solution and shaking at 25 °C for 1 h. An organic solution (5 mL) of the ligand (1.25×10^{-5} M) and an aqueous solution (5 mL) containing metal picrate (1.25×10^{-4} M) were shacked for 1 h. The resulting mixtures were allowed to stand for at least 1 h in order to complete the phase separation. The concentred of cation in aqueous phase was determined by atomic absorption spectro photometer. The extractability was calculated according to (1).

where A_0 is the concentration of cation in aqueous phase before extraction.

A is the concentration of cation in aqueous phase after extraction. The dependence of the distribution ratio D of the cation between the aqueous phase and the organic phase upon the ligand concentration was examined.

The general extraction equilibrium is given by equation (2)

$$M^{n+}_{aq} + npic_{aq+m} L_{org} = [M(Pic)_n(L)_m]_{org}$$
(2)

The overall extraction equilibrium constant is expressed as equation (3)

$$K_{ex} = \frac{[M(Pic)_{n}(L)_{m}]_{org}}{[M^{n+}]_{aq} [pic^{-}]^{n}_{aq} [L]^{m}_{org}}$$
(3)

The distribution ratio D would be defined by equation (4)

$$D = \frac{[M(Pic)_n(L)_m]_{org}}{[M^{n^+}]_{aq}}$$
(4)

It follows that

$$D = K_{ex} [pic^{-}]^{n}_{aq} [L]^{m} org$$
(5)

$$LogD = nlog[Pic] + log K_{ex} + m log[L]$$
(6)

The extraction aquilibrium constant (log K_{ex}) between an aqueous solution of metal picrates and an organic solution of (Schiff base cation) complex can be calculated from equation (6).

RESULT AND DISCUSSION

Macrocyclic Schiff bases

In this work, we have found that in the reaction between diethylene triamine or 2,2'-(ethylenedioxy)bis(ethylamine) and dialdehyde (I) the (2:2) Schiff base macrocycle is formed as the major product. The macrocyclic ligands were characterized by mass spectrometry, IR and ¹H and ¹³C NMR spectroscopy. The mass spectra of (II) and (III) play an important role in conforming the (2:2) (dialdehydes:diamine). Macrocyclic Schiff 1,12,15,18,29,32hexaaza-[3,4;8,9;20,21;26,27-tetra-(6'-methoxyphenyl)]-5,8,22,25-tetraoxacyclotetratriacosine-1,11,18,28-tetraen. (II) was synthesized by reaction of 1,4-bis(6-methoxy-2formylphenyl)-1,4-dioxa butane (I), with diethylene tri amine in methanol. The IR spectrum of the ligand (II) shows a peak due to v (CH=N)_{str} at 1640 cm⁻¹, a peak due to v (-N-H) at 3200 and the absence of a peak *due to* v (C=O) at around 1700 cm⁻¹ for the (I) is indicative of Schiff base condensation. The mass spectra show a molecular peak at m/z= 330 for (I) and m/z = 792 for (II) are confirmed the formation of macrocyclic Schiff base (II) 1,12,21,32-tetraaza-[3,4;9,10;23,24;29,30-tetra-(6'-methoxyphenyl)]-5,8,15,18,25,28,35,38-octaoxacyclo-tetracontane-1,11, 21,31-tetraene. (III) was synthesized by reaction of 1,4bis(6-methoxy-2-formylphenyl)-1,4-dioxabutane(I) with-2,2'-(ethylene dioxy)bis(ethylamine) in methanol. The IR spectrum of ligand (III) shows a v (CH=N)str peak at 1650 cm⁻¹ and the absence of a peak *due to* v (C= O) at around 1700 cm⁻¹ for the (I) is indicative of Schiff base condensation.¹³ The mass spectra show a molecular peak at m/z = 882 for (III) and m/z = 330 for (I) are confirmed the formation of macrocyclic Schiff base (III).

Extraction of metal picrates

Table (1) shows the extractability of Ag^+ and Cu^{2+} picrates from the aqueous phase into organic phase by macrocyclic Schiff bases (II) and (III). It is clear that the extractability results of the macrocyclic Schiff bases are different for both of the organic solvents, when dichloromethane was used as organic solvent macrocyclic (II) extracted Ag⁺ ion 78.0% but the other metal ions not extracted effectively. Macrocyclic (III) extracted Ag⁺ ion 89.2% for the same solvent. It is interesting that the percentage of the extraction of the metal ions with macrocyclic (III) is higher than of macrocyclic(II) for both of the solvents. These results is suggested that the phenyl group is the efficient group in the extraction and increasing a number of oxygen donor increases the percentage of the extraction of the metal ions. It can be seen from Table (1) that the solvent has an important effect upon the cation extractability. These results may depend on dielectric constants the solvents. The dielectric constants of dichloromethane and chloroform are 9.1 and 4.8 respectively. Dichloromethane having a high dielectric constants is favored for the extraction of all the metal ions there are similar results in literature.¹⁴ On the other hand, the better solvation of the complexes by dichloromethane may be a valuable reason for better extraction. From the extraction data shown in Table

Article

Table 1. The extractability of aqueous metal picrates for macrocyclic Schiff bases (II) and (III) in to organic phase at 25.0 ± 0.1 °C

Metal Ion	Extractability ^{a,b} %		Extractability ^{a,c} %	
	(II)	(III)	(II)	(III)
Ag^+	78.0 ± 0.3	89.2 ± 0.1	22.4 ± 0.1	42.2 ± 0.3
Cu ²⁺	25.1 ± 0.2	34.1 ± 0.3	8.1 ± 0.3	21.4 ± 0.2

^a Aqueous phase (5 mL); [pic] = 1.25×10^{-5} M,

Organic phase (5 mL), $[L] = 1.25 \times 10^{-4} M$

^b Defined as percent extracted in to dichloromethane phase

^c Defined as percent extracted in to chloroform phase

 Table 2. The selectivity of silver picrate over the other metal

 picrates for macrocyclic Schiff

Metal ion -	Selectivity ^{a,b} $D_{Ag^+}/D_m^{n^+}$		Selectivity ^{a,c} D_{Ag+}/D_m^{n+}	
	(II)	(III)	(II)	(III)
Cu ²⁺	9.1 ± 0.2	12.4 ± 0.3	4.8 ± 0.3	2.3 ± 0.2

^b Calculated for dichloromethane as organic phase

^c Calculated for chloroform as organic phase

(1). It is clear that the ligands which have N_6O_4 , N_4O_8 , donor sets show that both of the cation-cavity size and the type of binding sites in the ring contribute to the ability of Ag^+ ion binding.

Table (2) shows the selectivity of silver picrate over the other metal picrate for macrocyclic Schiff bases(II) and (III). The selectivity is indicated as $D_{Ag^+}/D_m^{n^+}$. D_{Ag^+} and $D_m^{n^+}$ denotes the distribution ratio of Ag^+ ion and M^{n^+} ion respectively. Macrocyclic Schiff bases (II) and (III) indicated high selective extraction of Ag^+ ion over the, Cu^{2^+} ion with 12.4, respectively. The selectivity results for to dichloromethane are higher than those for chloroform.

Fig. 1 shows the extraction into dichloromethane at different concentration of ligand from 1×10^{-5} M to 1.5×10^{-4} M. A liner relationship between Log D versus Log L is



Fig. 1. Log D versus Log L for the extraction of Agpicrate (■) and Cu-picrate (▲).

observed. The slope of equal to 1 suggesting the ligand (III) forms a (1:1) (L:M) for Cu^{2+} complexe with ligand (III). The slope of equal to 2 suggesting the ligand (III) forms a (1:2) (L:M) for Ag⁺ complexe with ligand (III).

CONCLUSION

A noval macrocyclic Schiff bases (II) and (III) have a good extraction abillity of Ag^+ ion from the aqueous phase to the dichloromethane phase.

But it was observed a high extraction of Ag^+ ion with macrocyclic Schiff base (III) wich has N_4O_8 donor sets than of macrocyclice (II) wich has N_6O_4 donor sets. It was found that macrocyclices have N_6O_4 , N_4O_8 donor sets extracted Ag^+ compared with the other transition metal cations Cu^{2+} as selective.

The composition of extracted complexes (L:M) is 2:1 when $M = Ag^+$ and 1:1 when $M = Cu^{2+}$ for the ligand (III).

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