



Synergistic Solvent Extraction of Copper (II) Ion by Using a Mixture of Imine Counting Benzedine and Palmitic or Salicylic Acid

Farouk Kandil, Amer Kasideh

Department of Chemistry, Faculty of Science, Damascus University, Damascus, Syria

Abstract In this research a new imine counting N_2O_5 donor atoms have synthesized. The new compound was prepared by reaction of 1,7-bis(6-methoxy-2-formyl phenyl)-1,4,7,10,14-penta-oxa-tetra-decane with benzedine. The imine was purified by chromatographic column filled with silicagel, eluted with chloroform. Identification of this imine: 1,21-Diaza-[3,4-18,19-di(6,6-methoxy phenyl)]-22, 29-benzedine-5,8,11,14,17-pentaoxa-cyclononaicocane 1,20-diene(II) was determined by 1H -NMR (LC-MS), (IR) spectroscopy. The liquid-liquid method carried out forextraction of metalsuch as $Pb_{(II)}$, $Ag_{(I)}$, $Cu_{(II)}$ in presence of picrate anion. Then we carried out synergistic solvent extraction of copper (II) ion by using a mixture of imine and palmitic or salicylic acid. Organic solvents chloroform and dichloromethane were investigated at $25 \pm 0.1^\circ C$ and using atomic absorption spectrometer. The extraction percentage was calculated.

Keywords Imine, Benzedine, Schiff Bases, Synergistic, Extraction

Introduction

Schiff-basemacrocycles have a great importance in macrocyclic and supra molecular chemistry [1]. In coordination chemistry the functionally substituted Schiff bases bearing additional donor groups represent the most important class of hetero polydentate ligands capable of forming mono-, bi-, and poly nuclear complexes with transition and non-transitionmetals [2]. They were among the first artificial metal macrocyclic complexes to be synthesized [3]. Interest in exploring metalion complexes with macrocyclic ligands has been continuously increasing owing to the recognition of the role played by these structures in metalloproteins [4]. A broad variety of Schiff macrocyclescan be utilized for metal biositesmodeling [5]. Expansion of our fundamental understanding of them amcrocyclization processes allows diversity of ligands to be synthesized as artificial cationic, anionic, and neutral guest receptors [6]. Macrocyclic compounds used in solvent extraction were mostly the oxygen donar type [7].A number of methods for the preparation of the large polyazamacrocyclic have been reported [8]. The most common synthetic procedure requires the use of N- tosyl groups to protect and activate the nitrogen atoms in the cyclization step [9].Ring closure occurs by acondensation reaction of N-tosylated polyamines with the appropriate ditosylate ester or dihalide in DMFin the presence of base [10]. These reactions allow the production of polyazamacrocycles in moderate yields, but removing the N- tosyl groups requires drastic conditions and is not always straightforward [11].Another cyclization process uses the template ring closure for formation of cyclic di- or tetra dental Schiff base [12]. 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 [13]. In some cases, reduction of the cyclic Schiff base and removal of the template ion have been difficult [14, 15]. A non template method for the formation of macro cyclic poly Schiff bases has also been studied [16]. This procedure often gave a polymeric material beside cyclization reaction, while there is no need to remove a metalion [17-19]. In the present work we used a non template method for the formation of two novelmacrocycles Schiff bases having: N_2O_2 , N_2O_4 donor atoms (II). The prepared compounds were used for removal of various metal ions from the aqueous phase in to the organic phase in liquid – liquid extraction system.

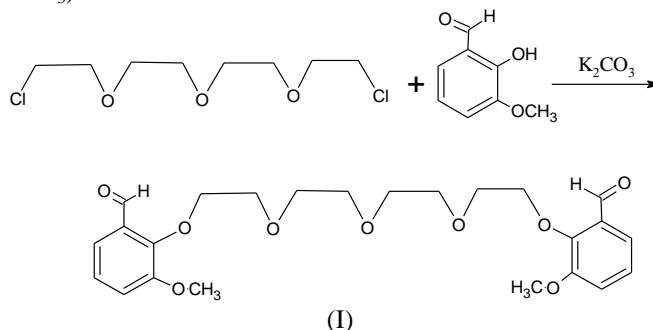


Materials and Methods

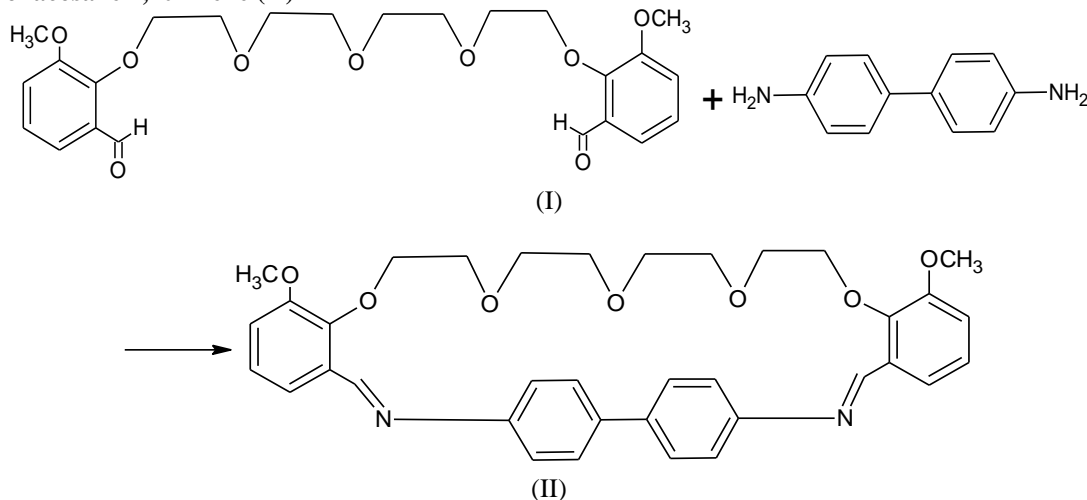
Chloroform, dichloromethane, dimethylformamide, acetonitrile, picric acid, methanol, K_2CO_3 , $Cu(NO_3)_2 \cdot 3H_2O$, $Ag(NO_3)$, $Pb(NO_3)_2 \cdot 6H_2O$, were analytical grade reagents and were purchased from Merck. Benzidine, *o*-vanillin, 1,11-dichloro-3,6,9-trioxadecane were obtained from Sigma-Aldrich. IR Spectra were recorded on Jasco 300 FT-IR Spectrophotometer using KBr discs. Mass spectra of the ligands were carried out using a micro mass Quattro LC-MS/MS Spectrometer. 1H -NMR spectra were recorded at ambient BRUKER AVANCE PX-400 Spectrometer. A Hitachi Model 180-80 Atomic absorption Spectrometer (acetylene/air flame) was used to determine the concentration of metal ions.

Synthesis of: 1,13 - Bis(6- Methoxy-2-Formylphenyl) -1, 4,7,10,13- BentaOxatriDecane(I)

To a stirred solution of *o*-vanillin (3.04g, 0.02mol) and K_2CO_3 (1.38g, 0.01mol) in DMF (50ml), 1,11-dichloro-3,6,9-trioxadecane (1.43g, 0.01mol) in DMF (10ml) was added dropwise, the reaction was continued for 10h at 150-155°C. The stirring was continued for 10h, an oily product began to separate from solution. It was purified by washing with ether. The large macrocyclic product was yellow oil. Yield: (3.4 g, 74%), Mass spectra: $m/z = 462$; IR (KBr pellets, cm^{-1}): 3000 (aromatic-CH), 2930-2887 (Aliphatic-C-H), 1710 (C=O)_{str}, 1482-1475 (aromatic C=C), 1289, 1311 (Ar-O), 1191 (O-CH₃).



Synthesis of: 1,21- Diaza- [3,4-18,19- di (6-Methoxy Phenyl)]-22, 29- Benzidine-5,8,11,14,17-Pentaoxa Cyclonacosane 1,20-Diene (II)



The macrocyclic compound (II) was prepared by dropwise addition of solution of the benzidine (1.840g, 0.010mol) in acetonitrile / methanol (50/50ml) to a stirred solution of compound (I) (0.460 g, 0.001mol) in acetonitrile / methanol (60 /40ml). 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 is pale yellow oil. Yield: (0.30g, 50%); Mass spectra: $m/z = 614$. IR (KBr pellets, cm^{-1}): (aromatic-CH), 2920-2847, 1633 (CH=N), 1238 (CH₂-O-CH₂), 1280 (C-O), 1190 (O-CH₃), 772 (substituted benzene).

1H -NMR ($CDCl_3$ -d₆): 1.38 – 1.98 (m, CH₂-CH₂), 2.5 (s, O-CH₃), 7.44 – 7.97 (m, Ar-H), 8.83 (s, CH=N), 4.34 – 4.22 (t, Ph-O-CH₂). Anal. Calc. For C₃₆H₃₈N₂O₇: C, 70.8; H, 6.27; N, 4.59. Found: C, 70.2; H, 6.33; N, 4.39.

Solvent Extraction

Transition metal picrates were prepared by the stepwise addition of a $1 \times 10^{-4} M$ of metal nitrate solution to a $1.0 \times 10^{-4} M$ aqueous picric acid solution and shaking at 25 °C for 1h. An organic solution (5 ml) of the ligand ($1.25 \times 10^{-4} M$)



and an aqueous solution (5 ml) containing metal picrate (1.25×10^{-5} M) were shaken for 1h. The resulting mixtures were allowed to stand for at least 1h in order to complete the phase separation. The concentration of cation in aqueous phase was determined by atomic absorption spectrometer.

$$X = \bar{X} \pm \frac{t.s}{\sqrt{n}}$$

$$\bar{X} = \frac{\sum_{i=1}^n (X_i)}{n} = \frac{1}{n} (X_1 + X_2 + X_3 + \dots + X_n)$$

$$S = \sqrt{\frac{\sum_{i=1}^n (X_i - \bar{X})^2}{n - 1}}$$

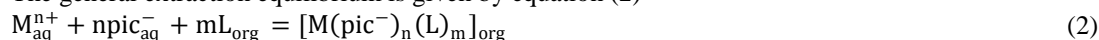
The extractability was calculated according to (1).

$$\%E = [(A_0 - A)/A_0] \times 100 \quad (1)$$

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)



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

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

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

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

It follows that

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

$$\log D = n \log [\text{Pic}^-]_{aq} + \log K_{ex} + m \log [L]_{org} \quad (6)$$

The extraction equilibrium 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

Reaction of benzedine and dialdehyde (I), forms a macrocycle schiff base in (1:1) as the major product. The macrocyclic ligand was characterized by mass spectrometry, IR and ^1H NMR spectroscopy. The mass spectra of (II) conform the formation of the compound Schiff base: 1,21- diaza- [3,4-18,19- di (6-methoxy phenyl)]-22, 29-benzedine-5,8,11,14,17-pentaoxa cyclononacosene 1,20-diene(II). The prepared compound was synthesized by reaction of 1,13 - bis (6- methoxy-2-formylphenyl) -1, 4,7,10,- bentaotridecane(I) with benzedine under highly diluted methanol/ acetonitrile. IR spectrum of the ligand (II) shows a peak due to ν (CH=N) at 1633 cm^{-1} and the absence of a peak due to ν (C=O) at 1710 cm^{-1} for (I) indicates of Schiff base formation. The mass spectra show a molecular peak at $m/z = 462$ for (I) and $m/z = 614$ for (II) which confirmed the formation of macrocyclic Schiff base (II). The NMR spectrum of the ligand (II) indicate the absence of formyl and amino groups which indicate the formation of the imine compound.

Extraction of Metal Picrates

Effect of Solvent on Extraction of Metal Picrates

Table (1) shows the extractability of $\text{Pb}_{(II)}$, $\text{Cu}_{(II)}$ and $\text{Ag}_{(I)}$ picrates from the aqueous phase into organic phase by macrocyclic Schiff base (II).

Table 1: The extractability of aqueous metal picrates for macrocyclic Schiff bases (II) in to organic phase $25.0 \pm 0.1^\circ\text{C}$.

Metal Ion	Extract ability ^b (II)	Eextract ability ^c (II)
$\text{Pb}_{(II)}$	60.7 ± 0.2	41.8 ± 0.5
$\text{Cu}_{(II)}$	22.4 ± 0.8	23.8 ± 0.6
$\text{Ag}_{(I)}$	75.4 ± 0.2	51.0 ± 0.1

^aaqueous phase (5ml); $[\text{pic}] = 1.0 \times 10^{-5} \text{ M}$, organic phase (5ml), $[L] = 1.0 \times 10^{-4} \text{ M}$

^bdefined as percent extracted into dichloromethane phase

^cdefined as percent extracted into chloroform phase



It is clear that the extractability results of the macrocyclic Schiff base are different for both of the organic solvents. When dichloromethane was used as organic solvent macrocyclic (II) extracted Pb_(II) ion 60.7%, Zn_(II) ion 75.4% Ag_(I) ion but the Cu_(II) metal ion was not extracted effectively. 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 of the solvents. The dielectric constants of dichloromethane and chloroform are 9.1 and 4.8 respectively. Dichloromethane with higher dielectric constants is favored for the extraction of all the metal ions there. On the other hand, the better solvation of the complexes by dichloromethane may be a valuable reason for better extraction.

Effect of Shaking Time on Extraction of Metal Picrates

The time which the equilibrium takes to establish during extraction of Pb_(II), Cu_(II) and Ag_(I) from aqueous phase to organic phase with macrocyclic Schiff base II in chloroform was depended on the metal ion

(Fig. 1.) Shows that at the same concentration of macrocyclic Schiff base(II) the extraction equilibrium is reached to 25 minutes for Cu_(II), 50 minutes for Pb_(II), and 50 minutes for Ag_(I)

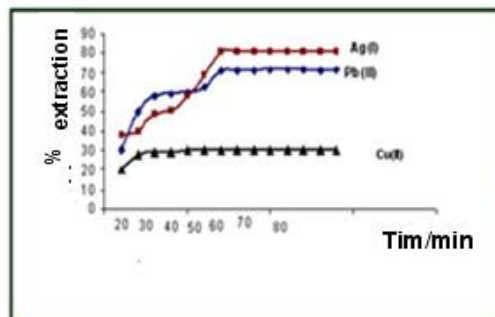


Figure 1: Effect of the time on extraction Pb, Cu and Ag picrate from aqueous phase to organic phase.

Effect of Concentration of Macrocyclic Schiff Base (II) on Extraction of Metal Picrates

The plot of $\log[D]$ 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 equation (3). The results of the experiments at the different concentration of macrocyclic Schiff base (II) gave the composition of extracted complex, it is found to have (L:M) ratio as 1:1 for Pb_(II), Ag_(I) ions and Cu_(II) ion. Fig. 2.

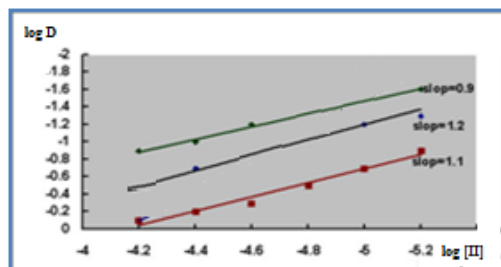


Figure 2: $\log[D]$ versus $\log [II]$ for the extraction of Ag, Pb, Cu picrate

Extraction of Copper_(II) in Chloroform with Mixture of (II) Schiff Base and Palmitic and Salicylic Acid

Table (2) shows the absence of the synergistic effect of (palmitic or salicylic acid) on the extractability of the Schiff base extractant for Cu_(II) ion is 22.4% with (II), the extraction increases to 80.3% with mixture of (II) and palmitic acid, 80.8% with mixture of (II) and salicylic acid.

Table (2): Synergistic copper extraction into a chloroform solution containing the mixture of Schiff bases (II) and palmitic or salicylic acid

	Extractability II
palmitic acid alone	-
salicylic acid alone	-
Schiff base alone (II)	22.4
Schiff base (II) + palmitic acid	80.3
Schiff base (II) + salicylic acid	80.8

aqueous phase (5ml); [pic] = $1. \times 10^{-4}$ M, organic phase (5ml), [L] = $1. \times 10^{-4}$ M, acid = $1. \times 10^{-4}$

Effect of Concentration of Palmitic Acid

The effect of palmitic acid concentration was studied from 0.5×10^{-4} M to 2.5×10^{-4} M by measuring the extraction of copper into a chloroform solution. The results of the experiments at the different concentration of palmitic acid and



macrocyclic Schiff base (II) gave the composition of extracted complex, It is found to have (Schiff bases/ palmitic acid) ratio as 1:1 for extraction of copper. Fig. 3.

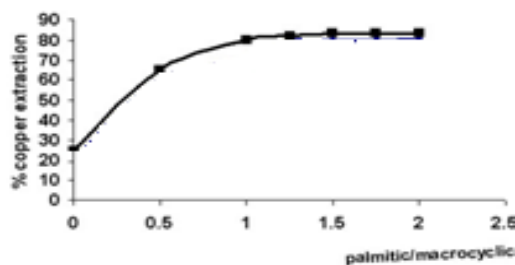


Figure 3: The effect of palmitic acid concentration on extraction of copper

Conclusions

The high transfer of $\text{Ag}_{(I)}$, $\text{Pb}_{(II)}$ ions from the aqueous phase to the dichloromethane phase was observed with macrocyclic Schiff base (II). It was found that macrocycles having N_2O_5 donor sites extracted $\text{Ag}_{(I)}$, $\text{Pb}_{(II)}$, preferably than $\text{Cu}_{(II)}$ metal ion, the extraction of copper was increasing when used mixture of (II) and palmitic acid or salicylic acid (synergistic effect).

The composition of extracted $\text{Cu}_{(II)}$, $\text{Pb}_{(II)}$, $\text{Ag}_{(I)}$ complex was (1:1) (L:M) for the ligand (II).

Acknowledgements

I am grateful to Department of Chemistry, Faculty of Sciences, Damascus University, Syria for the support of this research.

References

- Godoy-Alcántar, C., Yatsimirsky, A. K., & Lehn, J. M. (2005). Structure-stability correlations for imine formation in aqueous solution. *Journal of physical organic chemistry*, 18(10), 979-985.
- Zhou, H., Peng, Z. H., Pan, Z. Q., & Li, D. C. (2005). B. liu, Z. Zhang, RA Chi. *J. Mol. Struct*, 743, 59-68.
- Korupoju, S. R., & Zacharias, P. S. (1998). New optically active hexaaza triphenolic macrocycles: synthesis, molecular structure and crystal packing features. *Chemical Communications*, (12), 1267-1268.
- Borisova, N. E., Reshetova, M. D., & Ustynyuk, Y. A. (2007). Metal-free methods in the synthesis of macrocyclic Schiff bases. *Chemical reviews*, 107(1), 46-79.
- Martell, A. E., Perutka, J., & Kong, D. (2001). Dinuclear metal complexes and ligands: stabilities and catalytic effects. *Coordination Chemistry Reviews*, 216, 55-63.
- Di Bella, S. (2001). Second-order nonlinear optical properties of transition metal complexes. *Chemical Society Reviews*, 30(6), 355-366.
- Gallant, A. J., Hui, J. K. H., Zahariev, F. E., Wang, Y. A., & MacLachlan, M. J. (2005). Synthesis, structure, and computational studies of soluble conjugated multidentate macrocycles. *The Journal of organic chemistry*, 70(20), 7936-7946.
- V. Kuzmin, V. Lozitsky, G. Kamalov, R. Lozitskaya, A. Zheltvay, A. Fedtchouk, D. Kryzhanovsky, *Acta Biochim. Polonica* 47(2000) 867.
- Gao, J., Woolley, F. R., & Zingaro, R. A. (2005). In vitro anticancer activities and optical imaging of novel intercalative non-cisplatin conjugates. *Journal of medicinal chemistry*, 48(23), 7192-7197.
- R. Lozyska, D. Kryzhanovsky, A. Mazepa, V. Gorodniuk, Lozitsky, V.; A. Fedchuck, S. Rybalko, S. Diadium,; *J. Arkivoc* (2004) 118.
- Sessler, J. L., Katayev, E., Pantos, G. D., & Ustynyuk, Y. A. (2004). Synthesis and study of a new diamidodipyrromethane macrocycle. An anion receptor with a high sulfate-to-nitrate binding selectivity. *Chemical communications*, (11), 1276-1277.
- Nelson, S. M. (1980). Developments in the synthesis and coordination chemistry of macrocyclic Schiff base ligands. *Pure and Applied Chemistry*, 52(11), 2461-2476.
- Radecka-Paryzek, W., Patroniak, V., & Lisowski, J. (2005). Metal complexes of polyaza and polyoxaaza Schiff base macrocycles. *Coordination chemistry reviews*, 249(21), 2156-2175.
- Brooker, S. (2002). Some Copper and Cobalt Complexes of Schiff-Base Macrocycles Containing Pyridazine Head Units. *European Journal of Inorganic Chemistry*, 2002(10), 2535-2547.
- Martell, A. E., Perutka, J., & Kong, D. (2001). Dinuclear metal complexes and ligands: stabilities and catalytic effects. *Coordination Chemistry Reviews*, 216, 55-63.



16. Ümmühan, O. C. A. K., Hakan, A. L. P., Pinar, G. Ö. K. C. E., & Mirac, O. C. A. K. (2006). The synthesis of new N2S2-macrocyclic schiff base ligands and investigation of their ion extraction capability from aqueous media.
17. Guerriero, P., Tarnburini, S., & Vigato, P. A. (1995). From mononuclear to polynuclear macrocyclic or macroacyclic complexes. *Coordination Chemistry Reviews*, 139, 17-243.
18. Vigato, P. A., & Tamburini, S. (2004). The challenge of cyclic and acyclic Schiff bases and related derivatives. *Coordination Chemistry Reviews*, 248(17), 1717-2128.
19. Callaway, W. B., Veauthier, J. M., & Sessler, J. L. (2004). Schiff-base porphyrin and expanded porphyrin analogs. *Journal of Porphyrins and Phthalocyanines*, 8(01), 1-25.

