

Synthesis, Characterization and Metal Picrate Extraction Studies of Salicylaldehyde Derived Macrocyclic Schiff Bases

Misbah Ur Rehman¹, M. Imran^{2*}, M. Arif² and M. Farooq³

¹Institute of Chemical Science, Gomal University, D.I. Khan, KPK, 29050, Pakistan.

²Institute of Chemical Sciences, Bahauddin Zakariya University, Multan, 60800, Pakistan.

³Department of Chemistry, Govt. College Gujranwala, 52250, Pakistan.

Authors' contributions

This work was carried out in collaboration between all authors. All authors contribute equally for literature review, designing the study, experimental work and manuscript preparation.

Original Research Article

Received 30th November 2013
Accepted 24th December 2013
Published 14th January 2014

ABSTRACT

Three novel Salicylaldehyde derived macrocyclic Schiff bases were synthesized and well characterized by Elemental analyses, IR, Mass and ¹HNMR spectral data. The liquid-liquid extraction of metal cations (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 extraction was investigated at 25±0.1°C by using atomic absorption spectrometer.

Keywords: *Macrocyclic Schiff bases; metal cation extraction; solvent partitioning.*

1. INTRODUCTION

Schiff base are an important class of ligands due to not only their useful physical and chemical properties but also for the biological importance [1,2]. Over the past few years macrocyclic Schiff base ligands have received vital attention not only because of their pharmacological properties [3,4], soft-hard donor character and coordination behavior [5,6],

*Corresponding author: Email: imran345@hotmail.com;

but also for their capacity for chemical recognition of anions and metals of biochemical and environmental importance [7,8]. Heteroatom containing such as Nitrogen based macrocyclic bases showed similar mode of metal incorporation as metallo proteins have shown in which the requisite metal ion is bound in a macrocyclic cavity or cleft produced by the conformational arrangement of the protein [9]. Metal ions have enormous importance in many biological processes, but the increased concentration of metal ions especially heavy metal ions exerts toxic effects on living system [10]. Therefore, separation and determination of metal ions in environmental sources and living organisms play an important role for the sustainability of healthy life [11]. The need for the extraction of such metal ions encourages the synthetic chemists for synthesizing such macrocyclic compounds having effective extractability [12]. Macrocyclic Schiff base ligands showed good extraction abilities for the removal of different metal ions [13,14]. In this work we report three new macrocyclic Schiff bases and studied their properties for the extraction of Ag^+ and Cu^{2+} ions using different organic solvents.

2. EXPERIMENTAL DETAILS

2.1 Materials and Physical Measurements

All the reagents and solvents were purchased from Sigma-Aldrich and they were used as received. Reactions were monitored by thin layer chromatography (plates coated with 0.2 mm Merck 60 F254 silica gel) and were visualized by UV irradiation (254 nm). Elemental analyses were carried out with a LECO-CHNS-9320 model. ^1H NMR spectra of compounds were recorded with a Bruker Spectrospin Avance DPX-400 using TMS as internal standard and d_6 DMSO as solvent. Infrared spectra of compounds were recorded on a Philips Analytical PU 9800 FTIR spectrophotometer. The melting points of compounds were determined with a Gallenkamp melting point apparatus. Electron impact mass spectra (EIMS) were recorded on a JEOL MS Route instrument. A Hitachi Model 180-80 Atomic absorption Spectrometer (acetylene/air flame) was used to determine the concentration of metal ions.

2.2 Synthesis of 2, 2'-(ethane-1,2-diylbis(oxy)) Dibenzaldehyde

To a solution of salicylaldehyde (0.2 mol) and K_2CO_3 (0.1 mol) in DMF (100 cm^3) was added drop wise 1,2-dichloroethane (0.1 mol) in DMF (40 cm^3). The reaction mixture was allowed to stir for 10 h at $150\text{--}155^\circ\text{C}$ and then 5 h at room temperature. After the addition was completed then 200 cm^3 distilled water was added and was placed in refrigerator. Then, after 1 h precipitates were collected, washed with water dried and recrystallized through ethanol (Fig. 1).

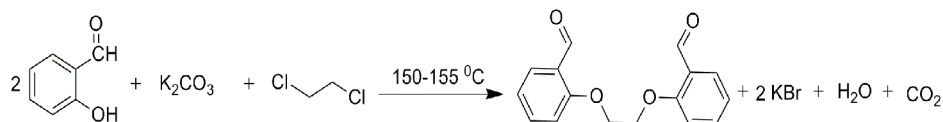


Fig. 1. Synthesis of 2, 2'-(ethane-1,2-diylbis(oxy)) dibenzaldehyde

2.3 Synthesis of Schiff Bases

To a methanolic solution of 2,2'-(ethane-1,2-diylbis(oxy)) dibenzaldehyde (0.2 mole) was added respective primary amine (0.2 mole). Mixture was refluxed for 3 hours, precipitates were formed. The completion of reaction was confirmed by TLC. Precipitates were cooled to room temperature, filtered, washed with methanol and dried in oven (Fig. 2).

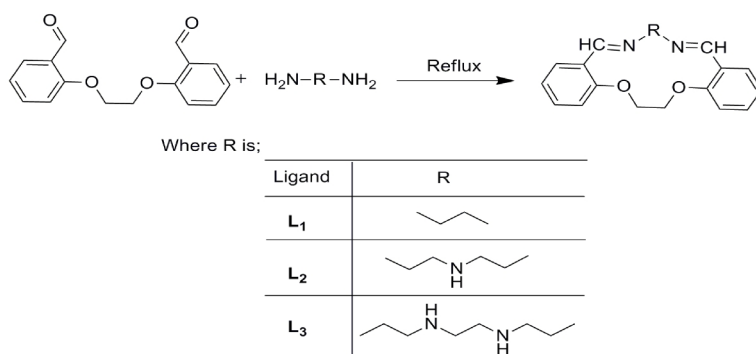


Fig. 2. Synthesis of Schiff bases (L₁-L₃)

2.4 2, 2'-(ethane-1,2-diylbis(oxy)) dibenzaldehyde

Bright brown solid, Yield: 80%, m.p: 104°C; IR (KBr cm⁻¹): 3112 (Ar-CH), 2948, 2821 (Aliph.-CH), 1675 (C=O), 1485, 1461 (Ar-C=C), 1281, 1231 (Ar-O); Mass spectrum (ESI) [M]⁺: 270; Anal Calcd. for C₁₆H₁₄O₄ (%): C, 71.10; H, 5.22; O, 23.68. Found (%): C, 71.01; H, 5.02; O, 23.53.

2.5 Compound 1 (L₁): (5E,9E)-7,8,16,17-tetrahydro dibenzo [e,m] [1,4,8,11] dioxadiazacyclotetradecine

Reddish brown solid; yield: 78%; m.p; 121°C; IR (KBr cm⁻¹): 3018 (Ar-CH), 2928 (Aliph-CH), 1669 (C=N), 1655 (Ar-C=C), 1245 (Ar-O); ¹H-NMR (DMSO-d₆): δ 3.95 (m, 4H, N-CH₂), 4.24 (m, 4H, O-CH₂), 7.13 (m, 2H, Benzene ring), 7.21 (d, 2H, Benzene ring), 7.47 (m, 2H, Benzene ring), 7.63 (d, 2H, Benzene ring), 8.12 (s, 2H, N=CH-); Mass spectrum (ESI) [M]⁺=294; Anal. Calcd. for C₁₈H₁₈N₂O₂ (%): C, 73.45; H, 6.16; N, 9.52; O, 10.87. Found (%): C, 73.41; H, 6.13; N, 9.50; O, 10.74.

2.6 Compound 2 (L₂): (5E,12E)-8,9,10,11,19,20-hexahydro-7H-dibenzo [e,p] [1,4,8,11,14] dioxatriazacycloheptadecine

Yellow solid; yield: 68%; m.p: 147°C; IR (KBr cm⁻¹): 3038 (Ar-CH), 2916 (Aliph-CH), 1685 (C=N), 1625 (Ar-C=C), 1268 (Ar-O); ¹H-NMR (DMSO-d₆): δ 2.81 (m, 4H, N-CH₂), 3.62 (m, 4H, =N-CH₂), 4.46 (m, 4H, O-CH₂), 7.02 (m, 2H, Benzene ring), 7.47 (d, 2H, Benzene ring), 7.69 (m, 2H, Benzene ring), 7.92 (d, 2H, Benzene ring), 8.1 (s, 2H, N=CH-); Mass spectrum (ESI) [M]⁺ = 337; Anal. Calcd. for C₂₀H₂₃N₃O₂ (%): C, 71.19; H, 6.87; N, 12.45; O, 9.48. Found (%): C, 71.12; H, 6.81; N, 12.37; O, 9.42.

2.7 Compound 3 (L₃): (5E,15E)-7,8,9,10,11,12,13,14,22,23-decahydro dibenzo [e,s] [1,4,8,11,14,17] dioxatetraazacycloicosine

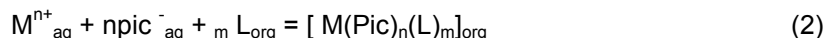
Black solid; yield: 74%; m.p: 180°C; IR (KBr cm⁻¹): 3010 (Ar-CH), 2933 (Aliph-CH), 1595 (C=N), 1675 (Ar-C=C), 1230 (Ar-O); ¹H-NMR (DMSO-d₆): δ 2.61 (m, 4H, HN-CH₂-CH₂-NH), 2.83 (m, 4H, N-CH₂), 3.52 (m, 4H, =N-CH₂), 4.42 (m, 4H, O-CH₂), 7.13 (m, 2H, Benzene ring), 7.21 (d, 2H, Benzene ring), 7.42 (m, 2H, Benzene ring), 7.66 (d, 2H, Benzene ring), 8.15 (s, 2H, N=CH-); Mass spectrum (ESI) [M]⁺ = 380; Anal. Calcd. for C₂₂H₂₈N₄O₂ (%): C, 69.45; H, 7.42; N, 14.73; O, 8.41. Found (%): C, 69.42; H, 7.32; N, 14.62; O, 8.37.

2.8 Solvent Extraction

Ag⁺ and Cu²⁺ picrates were synthesized by the addition of metal nitrate solution (1×10⁻² M) to aqueous picric acid solution (1.25×10⁻⁴ M) and then shake this mixture for 1h at 25°C. Then, 5ml organic solution of 1.25×10⁻⁵ M containing macrocyclic Schiff base was allowed to mix with 5ml aqueous solution of 1.25×10⁻⁴ M containing Ag⁺ and Cu²⁺ picrate. The mixture was shaken well and then to allowed to stand for 1 h to complete the extraction. Aqueous and organic phase were separated and concentration of cation were determined in aqueous phase using atomic absorption spectrophotometer. The extractability was calculated using equation (1).

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

Where; E is the extractability, A₀ is cation concentration before extraction and A is the cation concentration after extraction in aqueous medium. 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 concentration of ligand was ranged between 1×10⁻⁵ M to 5×10⁻⁴ M. The general extraction equilibrium is given by equation (2)



The following logarithmic expression is valid for the above extraction system.

$$\text{Log} D = n \text{log}[\text{Pic}] + \text{log} K_{ex} + m \text{log}[L] \quad (3)$$

log K_{ex} is the extraction equilibrium constant between an aqueous solution of metal picrates and an organic solution of Schiff base-cation complex, which can be calculated from equation (3).

3. RESULTS AND DISCUSSION

3.1 Macrocyclic Schiff Bases

3.1.1 IR spectra

In the IR spectrum of reactants, NH₂ group of different amines was found in the region 3360-3400 cm⁻¹ and in aldehyde (C=O) band was observed in the region 1695-1715 cm⁻¹. In the IR spectrum of Schiff bases, these (C=O) and NH₂ bands were disappeared which indicates the formation of Schiff bases. The ligands showed a band at 1595-1685 cm⁻¹ assigned to ν(C=N) stretching vibrations which represent Schiff base formation. In the IR spectrum of the

Schiff bases, peaks of (Ar-C=C) and (Ar-CH) were observed in the region of 1625-1675 cm^{-1} and 3010-3038 cm^{-1} respectively which indicates that compound exists as whole and do not decompose or undergo side reactions [15].

3.1.2 ^1H NMR spectra

^1H NMR spectra of the ligands were recorded in DMSO-d_6 . The ^1H NMR spectral data along with the possible assignments is recorded in the Experimental. The ^1H NMR spectra of Schiff base exhibits singlet at 8.1-8.15 ppm due to $-\text{CH}=\text{N}$ proton [16]. In addition to this signal, Schiff bases (L_1 - L_3) have shown the peaks at 4.24-4.46 ppm due to methylene group connected to the oxygen atom [17]. Multiplet peaks at 7.02-7.92 ppm indicated the presence of benzene ring the ligands (L_1 - L_3) [18].

3.2 Extraction of Metal Picrates

The extractability of Ag^+ and Cu^{2+} picrates from the aqueous phase into organic phase by macrocyclic Schiff bases (L_1 - L_3) is shown in the Table 1. It has been seen that the extractability by the macrocyclic Schiff bases is different for both of the organic solvents. Dichloromethane is an efficient organic solvent for macrocyclic Schiff bases for metal picrate extraction. Dichloromethane showed extraction results 72.0%, 85.2% and 93.2% for macrocyclic Schiff bases L_1 , L_2 and L_3 respectively. It has also been shown that the percentage of the extraction of the metal ions with macrocyclic Schiff base L_3 is higher as compared to other macrocyclic Schiff bases L_1 and L_2 for both of the solvents, this is probably due to increase number of donor atoms in the macrocyclic Schiff base L_3 [19]. It is also seen that the solvent has an important effect upon the cation extractability and this is due to the difference in the dielectric constants of the solvents. The dielectric constants of dichloromethane is high (9.1) as compared to chloroform (4.8) which may be a favorable factor for the extraction of all the metal ions; there are similar results in the literature [20,21].

Table 1. The extractability of aqueous metal picrates for macrocyclic Schiff bases (L_1 - L_3) into organic phase at $25.0 \pm 0.1^\circ\text{C}$

Metal Ion	Extractability ^{a,b} %			Extractability ^{a,c} %		
	L_1	L_2	L_3	L_1	L_2	L_3
Ag^+	72.0 \pm 0.1	85.2 \pm 0.1	93.2 \pm 0.1	27.2 \pm 0.1	42.2 \pm 0.1	52.8 \pm 0.1
Cu^{2+}	28.1 \pm 0.1	39.1 \pm 0.1	57.2 \pm 0.1	11.9 \pm 0.1	27.6 \pm 0.1	37.2 \pm 0.1

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

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

b = Defined as percent extracted in to dichloromethane phase

c = Defined as percent extracted in to chloroform phase

The selectivity of silver picrate over the other metal picrate for macrocyclic Schiff bases (L_1 - L_3) is shown in the Table 2. The selectivity is indicated as $D_{\text{Ag}^+} / D_{\text{Cu}^{2+}}$. D_{Ag^+} and $D_{\text{Cu}^{2+}}$ denotes the distribution ratio of Ag^+ ion and Cu^{2+} ion respectively. Macrocyclic Schiff bases (L_1 - L_3) indicated high selective extraction of Ag^+ ion over the Cu^{2+} ions and high selectivity results for dichloromethane as compared to chloroform [22].

Table 2. The selectivity of silver picrate over the other metal picrates for macrocyclic Schiff bases (L₁-L₃)

Metal Ion	Selectivity ^{a,b} D_{Ag^+}/D_m^{n+}			Selectivity ^{a,c} D_{Ag^+}/D_m^{n+}		
	L ₁	L ₂	L ₃	L ₁	L ₂	L ₃
Ag ⁺	7.6±0.1	14.7±0.1	17.3±0.1	3.2±0.1	5.1±0.1	8.2±0.1

b = Calculated for dichloromethane as organic phase

c = Calculated for chloroform as organic phase

The extraction into dichloromethane at different concentration of the macrocyclic Schiff base L₃ is shown in Fig. 3. A liner relationship between Log D versus Log L is observed. It is found that the macrocyclic Schiff base L₃ form a complex with Cu²⁺ as 1:1 metal:ligand ratio and for Ag⁺ it is 2:1 [23] as described in Fig. 3.

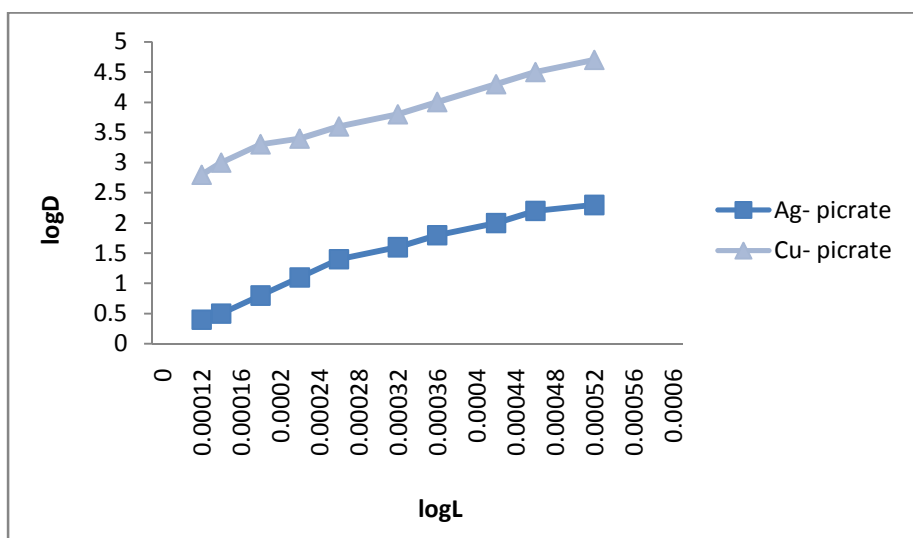


Fig. 3. Log D versus Log L for the extraction of Ag-picrate and Cu-picrate.

4. CONCLUSION

Three new macrocyclic Schiff bases (L₁-L₃) were prepared and studied their extraction ability for Ag⁺ and Cu²⁺ picrate. Macrocyclic Schiff base (L₃) with higher number of donor atoms has higher extraction ability as compared to others. Organic solvent with high dielectric constant also supports the extraction of metal picrate from aqueous phase into organic phase and it has been shown that dichloromethane showed good results as compared to chloroform. As for as the selectivity is concerned, it was seen that the all the macrocyclic Schiff base were more selective towards Ag⁺ ion. It was also observed that Ag⁺ form complex as 2:1 M:L ratio and Cu²⁺ as 1:1 M:L ratio.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Misbah ur Rehman, Imran M, Arif M. Synthesis, Characterization and *in vitro* Antimicrobial Studies of Schiff-Bases Derived from Acetylacetone and Amino Acids and their Oxovanadium(IV) Complexes. *Am J of Appl Chem*. 2013;1(4):59-66.
2. Arif M, Qurashi MMR, Shad MA. Metal-based antibacterial agents: synthesis, characterization, and *in vitro* biological evaluation of cefixime-derived Schiff bases and their complexes with Zn(II), Cu(II), Ni(II), and Co(II). *J of Coord Chem*. 2011;64(11):1914-1930.
3. Min W, Liu-Fang W, Yi-Zhi L, Qin-Xi L, Zhi-Dong X, Dong-Ming Q. Antitumour activity of transition metal complexes with the thiosemicarbazone derived from 3-acetylumbelliferone. *Trans Metal Chem*. 2001;26(3):307-310.
4. Abdullah MA, Salman AK. Synthesis and Anti-Bacterial Activities of Some Novel Schiff Bases Derived from Aminophenazone. *Molecules*. 2010;15(10):6850-6858.
5. Maji M, Ghosh S, Chattopadhyay SK, Wu BM, Mak TCW. Studies on Ru(II) complexes of 4-(4-tolyl) thiosemicarbazone of 2-acetylpyridine(LH). First synthesis and structural characterization of a Ru complex containing the imine(mpi). Crystal structure of [Ru(LH)(PPh₃)₂Cl]Cl·CH₂Cl₂ and [Ru(LH)(PPh₃)(mpi)]Cl₂·CH₂Cl₂·3H₂O. *J. Chem. Soc., Dalton Trans*. 1999;135-140.
6. Sengupta P, Dinda R, Ghosh S, Sheldrick WS. Synthesis and characterization of some biologically active ruthenium (II) complexes of thiosemicarbazones of pyridine 2-aldehyde and thiophene 2-aldehyde involving some ring substituted 4-phenylthiosemicarbazides and 4-Cyclohexylthiosemicarbazide. Crystal Structure of Cis-[Ru(PPh₃)₂(L⁶H)₂](ClO₄)₂·2H₂O [L⁶H=4-(Cyclohexyl) Thiosemicarbazone of Pyridine 2-Aldehyde]. *Polyhedron*. 2003;22(3):447-453.
7. Priyanka B, Om PP, Soumitra KS. Microwave-assisted synthesis, spectroscopy and biological aspects of binuclear titanocene chelates of isatin-2,3-bis(thiosemicarbazones). *Appl Organometallic Chem*. 2009;23(1):19–23.
8. Dimitra KD, Nikolaos K, Mavroudis AD, John RM, Christopher SF, John KS, Douglas XW. Trinuclear Palladium(II) Complexes with 2-Hydroxy-4-methoxyacetophenone *N*⁴-Dimethylthiosemicarbazone: Synthesis, Spectral Studies and Crystal Structure of a Tripalladium Complex. *Eur J of Inorg Chem*. 2000;2000(4):727-734.
9. Gao EQ, Sun HY, Liao DZ, Jiang ZH, Yan SP. Synthesis of and magnetic interactions in binuclear Cu(II)-M(II) (M=Cu, Ni and Mn) complexes of macrocyclic oxamido ligands. *Polyhedron*. 2002;21(4):359–364.
10. GD Christian. Analytical strategies for the measurement of lithium in biological samples. *J Pharm Biomed Anal*. 1996;14(8-10):899-908.
11. Ibrahim U, Ismet B, Turgut K, Umit C. Synthesis, complexation and antifungal, antibacterial activity studies of a new macrocyclic schiff base. *J of Heterocyclic Chem*. 2006;43(6):1679-1684.
12. Ummuhan O, Hakan A, Pinar G, Miraç O. The Synthesis of New N₂S₂-Macrocyclic Schiff Base Ligands and Investigation of Their Ion Extraction Capability from Aqueous Media. *Separation Sci and Tech*. 2006;41(2):391-401.

13. Souad K, Nadeem A, Farouk K. Synthesis of New Macrocyclic Schiff Base Ligands and Investigation of their Ion Extraction Capability from Aqueous Media. *Jordan J of Chem*. 2012;7(1):73-80.
14. Farouk K, Mohamad KC, Wail Al Z. Synthesis of Macrocyclic Bis-Hydrazone and Their Use in Metal Cations Extraction. *ISRN Org Chem*. Article ID 208284; 2012.
15. Nakamoto K. Infrared and raman spectra of inorganic and coordination compounds. 5th edn. John Wiley & Sons Inc New York; 1997.
16. Sayaji R. Synthesis, Magneto-Spectral and Biological studies of Manganese (II) complexes with Heteroaryl hydrazone. 2005;17(4):2663-2668.
17. Simons WW. The Sadtler handbook of proton NMR spectra. Sadtler Research Laboratories Inc Philadelphia; 1978.
18. Pasto DJ. Organic structure determination. Prentice Hall International London; 1969.
19. Zoubi WA, Kandil F, Chebani MK. Synthesis of Macrocyclic Schiff Bases Based on Pyridine-2,6-Dicarbohydrazide and their Use in Metal Cations Extraction. *Organic Chem Current Res*. 2012;1:104.
20. Berrin Z, Giray T, Sait E, Candan H, Halil H. Effect of structural modifications of diaza-18-crown-6 on the extractability and selectivity of univalent metal picrates. *Talanta*. 2001;53(5):1083-1087.
21. Karakuş, Ozlem, Deligoz, Hasalettin. Synthesis and characterization of three novel azocalix [4] arene Schiff base derivatives and their selective copper extraction. *Journal of the Iranian Chemical Society*. 2012;9(1):93-100.
22. Abe S, Fujii K, Sono. Liquid-liquid extraction of manganese (II), copper(II) and zinc(II) with acyclic and macrocyclic Schiff bases containing bisphenol A subunits. *T. Analytica Chimica Acta*. 1994;293(3):325-330.
23. Souad K, Farouk K, Nadeem A. Solvent Extraction of Ag(I) and Cu(II) with New Macrocyclic Schiff Bases. *J of the Chin Chemical Soc*. 2012;59(4):525-528.

© 2014 Rehman et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:

The peer review history for this paper can be accessed here:
<http://www.sciencedomain.org/review-history.php?iid=318&id=7&aid=3342>