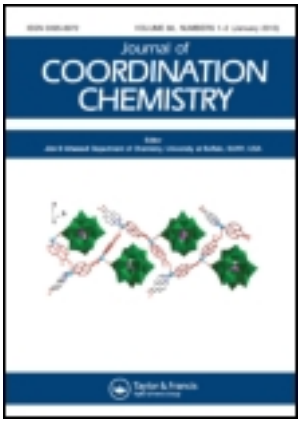
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:48
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Solvent extraction of metal ions by use of Schiff bases

Wail Al Zoubi [a]

[a] Faculty of Science, Department of Chemistry , University of Damascus , Damascus , Syria

Accepted author version posted online: 08 May 2013.Published online: 11 Jun 2013.

To cite this article: Wail Al Zoubi (2013) Solvent extraction of metal ions by use of Schiff bases, Journal of Coordination Chemistry, 66:13, 2264-2289, DOI: 10.1080/00958972.2013.803536

To link to this article: http://dx.doi.org/10.1080/00958972.2013.803536

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Journal of Coordination Chemistry, 2013
Vol. 66, No. 13, 2264–2289, http://dx.doi.org/10.1080/00958972.2013.803536

Downloaded by [Renmin University of China] at 10:48 13 October 2013

REVIEW

Solvent extraction of metal ions by use of Schiff bases

WAIL AL ZOUBI*

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

(*Received 13 February 2013; in final form 27 February 2013*)

Schiff bases are aldehyde or ketone like compounds in which the carbonyl group is replaced by imine or azomethine group. They are widely used for industrial purposes and also exhibit a broad range as extractants. A general view of solvent extraction applications of complexes is discussed in this review. The family of Schiff bases and their extraction of various transition metals such as Co, Cu, Cr, Fe, Ga, Hg, Mn, Mo and Ni are discussed. A brief history of the synthesis and reactivity of Schiff bases will be presented. Factors on solvent extraction will be illustrated and discussed.

Keywords: Schiff bases; Solvent extraction; Metal cations; Preconcentration

1. Introduction

A Schiff base (imine or azomethine), named after Hugo Schiff, contains a carbon-nitrogen double bond with the nitrogen connected to an aryl or alkyl but not hydrogen. Schiff bases are of general formula $R_1R_2C{=}NR_3$, where R_3 is a phenyl or alkyl group that makes the Schiff bases a stable imine. Schiff base compounds were reported for the first time by Hugo Schiff in 1864 [1].

These bases are very efficient as ligands. Many Schiff bases have a second functional group, generally an OH, near the imine function. This proximity of the functional groups permits the formation of five or six member chalate rings when coordinated with metal ions. Schiff bases have a diversified structure with nitrogen and oxygen donor systems being the most numerous. However nitrogen and sulfur donor systems and only nitrogen systems have been studied [2]. Due to the various synthetic procedures, numerous Schiff bases of various structural types have been synthesized. Probably the best known Schiff base is *N*,*N*′-ethylenebis(salicylideneiminato) or salen, which is a bifunctional and tetradentate(ONNO) ligand. The more general term salen-type is used in the literature to describe the class of [O, N, N, O] bis-Schiff base ligands. The properties of salen-type ligands can be altered by fine-tuning the electronic and steric effects of substituent groups [3].

Schiff bases are widely used as pigments and dyes, catalysts, intermediates in organic synthesis, and as polymer stabilizers [4]. Schiff bases have also been shown to exhibit a broad range of biological activities, including antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic properties [5–8].

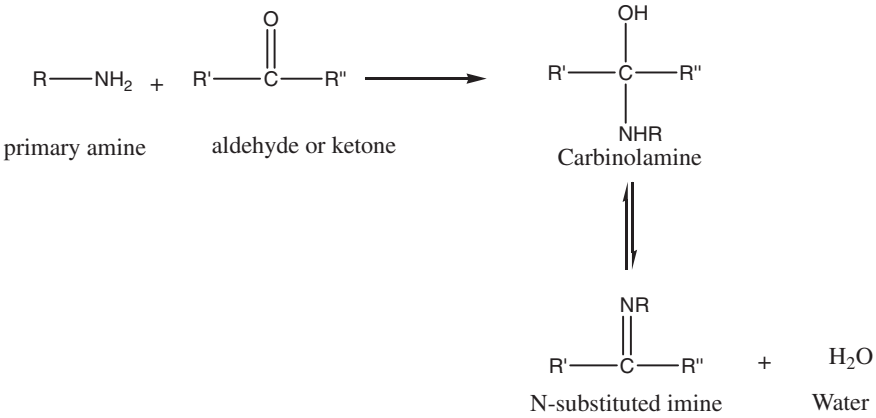
*Email: wwailalzoubi@yahoo.com

© 2013 Taylor & Francis

2. Preparation of Schiff bases

A Schiff base is the nitrogen analog of an aldehyde or ketone in which the C=O is replaced by a C=N-R group. It is usually formed by condensation of an aldehyde or ketone with a primary amine according to the following scheme (figure 1):
where *R* may be an alkyl or an aryl group. Schiff bases that contain aryl substituents are more stable and more readily synthesized, while those which contain alkyl substituents are relatively unstable. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerizable, while those of aromatic aldehyde having effective conjugation are more stable [9–15].

The formation of Schiff bases from aldehydes or ketones is a reversible reaction and generally takes place under acid or base catalysis, or upon heating.



The formation is generally driven to completion by separation of the product or removal of water, or both. Many Schiff bases can be hydrolyzed back to their aldehydes or ketones and amines by aqueous acid or base.

The mechanism of Schiff base formation is another variation on the theme of nucleophilic addition to the carbonyl group. In this case, the nucleophile is the amine. In the first part of the mechanism, the amine reacts with the aldehyde or ketone to give an unstable addition compound called a carbinolamine.

The carbinolamine loses water by either acid or base catalyzed pathways. Since the carbinolamine is an alcohol, it undergoes acid catalyzed dehydration.

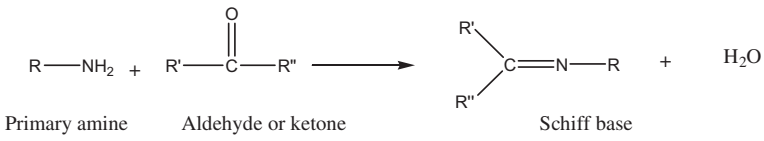
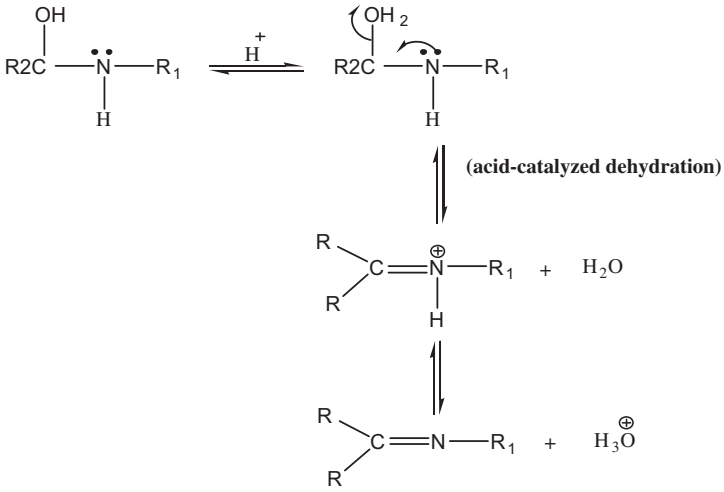


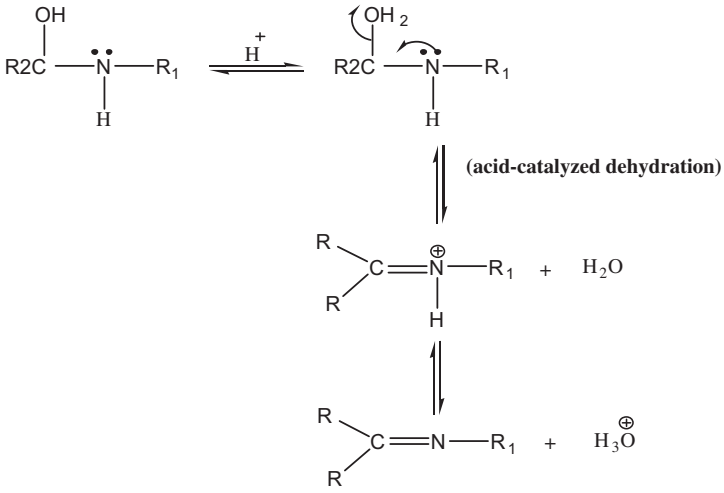
Figure 1. Synthesis scheme for the preparation of the Schiff bases.

Downloaded by [Renmin University of China] at 10:48 13 October 2013



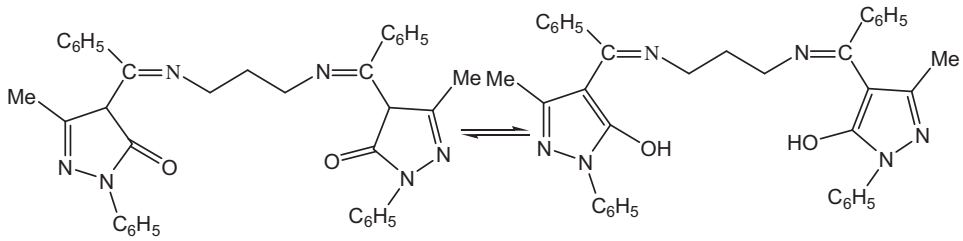
Typically the dehydration of the carbinolamine is the rate-determining step of Schiff base formation and this is why the reaction is catalyzed by acids. Yet the acid concentration cannot be too high because amines are basic compounds. If the amine is protonated and becomes non-nucleophilic, equilibrium is pulled to the left and carbinolamine formation cannot occur. Therefore, many Schiff base syntheses are carried out at mildly acidic pH.

The dehydration of carbinolamines is also catalyzed by base. This reaction is somewhat analogous to the E_2 elimination of alkyl halides except that it is not a concerted reaction. It proceeds in two steps through an anionic intermediate.



Schiff base formation is really a sequence of two types of reaction, i.e. addition followed by elimination [16].

Downloaded by [Renmin University of China] at 10:48 13 October 2013



Scheme 1. The enol-keto tautomerism of H_2A.

Downloaded by [Renmin University of China] at 10:48 13 October 2013

3. Solvent extraction of metal ions by Schiff bases

Solvent extraction of metal ions has been used for a long time for separation and determination of metal ions. The first quantitative description of the extraction process was, however, not made until 1941 when Kolthoff and Sandell [17] compared experimental data with theoretical predictions for the extraction of metal dithizonates. They found that the theory they proposed was valid under wide experimental conditions. However, the systems used by Kolthoff and Sandell were simple ones and hence relatively simple theory was used to successfully explain their behavior. In practice solvent extraction systems are complicated by other factors, e.g. hydrolysis, polymerization and complex formation in aqueous phase. It has subsequently become apparent that such factors have an important influence on the solvent extraction of chelates. Several authors [18–24] have published reports since 1941 on the theory of solvent extraction of metal chelates which take these factors into account. In particular two publications by Irving, Rossotti and Williams [25] and Stary [26] should be noted for their comprehensive treatment of the subject.

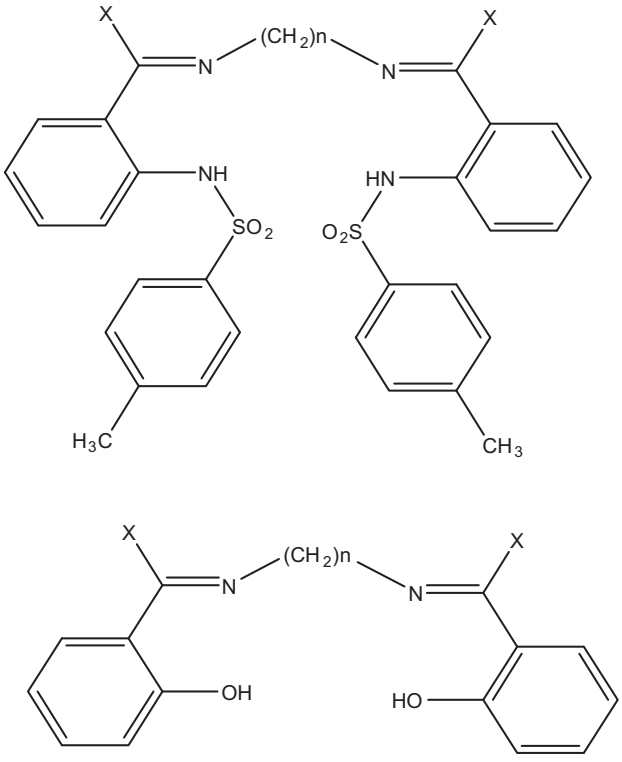
Copper, cobalt and nickel are both vital and toxic for many biological systems [27, 28]. Thus, determination of trace amounts of Cu, Co and Ni is increasingly important because of the increased interest in environmental pollution. Flame and graphite furnace atomic absorption spectrometry and spectrophotometric methods provide accurate and rapid determination of these metals in natural waters and wastewaters. Nevertheless, for the extremely low concentration of these metals in water, a direct determination cannot be applied without previous preconcentration and separation. The most widely used techniques for separation and preconcentration of trace amounts are liquid–liquid extraction [29], precipitation, sorption [30, 31], solid phase techniques [32] and chelating resins [33]. Very often, both separation and preconcentration are required, and an advantage of solvent extraction is that both can be obtained in the same step [34]. Recovery of metals from an aqueous phase by solvent extraction is achieved by contacting the aqueous phase with an organic phase that contains a metal selective chelating agent dissolved in a diluent [35]. For extraction of metal ions, it is preferable that the chelating agent used has high distribution coefficient and pH dependence in the system chosen. Reagents such as crown ethers, Schiff bases, oximes, amines and several phosphine oxides can be used as chelating agents [36–41].

3.1. *Multidentate nitrogen/oxygen donor Schiff bases*

Schiff bases bearing nitrogen/oxygen donors have been shown to exhibit interesting ionophoric properties, in particular towards heavy metal ions. These properties were investigated using different techniques and methods. Binding abilities of some Schiff base

ligands towards transition metal ions have been recently evaluated using UV–vis. and potentiometric methods [42].

Schiff bases are interesting chelating agents. *N*,*N*′-bis[l-phenyl-3-methyl-5-hydroxypyrazole-4-benzylidenyl]-1,3-propylene diamine (H_2A) (scheme 1) was synthesized and characterized. The extraction of palladium(II) from HNO_3 or $HClO_4$ with H_2A in chloroform or toluene was investigated. The influences of the Schiff base concentration in the organic phase, the pH and anions (Cl^-, SO_4^{2-}, NO_3^-, ClO_4^-) in the aqueous phase and temperature on the distribution ratio for palladium(II) have been examined. In this work, the percent palladium extraction (*E*) was larger than (the percent palladium extraction (*E*)) 98% when pH > 2; *E* decreased with increase of acidity when pH < 2.0. Also the extraction of palladium in nitric, sulfuric of perchloric acid media is better than that in hydrochloric acid solution. The distribution ratio depends on the equilibrium concentration of the extractant in the organic phase, extraction increases at higher reagent concentration and the extraction curve shifts to more acidic pH values. The effect of temperature on the extraction of palladium was studied. An increase in temperature resulted in a decreased extraction of



n	X	Sulfonamide-type (upper)	Phenol-type (lower)
2	C_6H_5	H_2tsben-Ph_2	H_2salpn-Ph_2
2	CH_3	H_2tsben-Me_2	H_2salen-Me_2
3	C_6H_5	H_2tsben-Ph_2	H_2salpn-Ph_2
3	CH_3	H_2tsbpn-Me_2	H_2salpn-Me_2

Figure 2. Chemical structure of di-Schiff base ligands used in this study.

Downloaded by [Renmin University of China] at 10:48 13 October 2013

palladium. This decrease may be due to decrease in the distribution constant of HA and the increase in the dissociation constant of the extractant. The van't Hoff equation in the form given by equation (l) can be used to calculate the overall enthalpy change, ΔH, associated with the extraction of palladium by H_2A in chloroform [43].

$$\frac{\log D}{(1/T)} = \frac{-\Delta H}{2.303R} \tag{1}$$

Also the extraction of palladium(II) with H_2A was as follows:

$$pd(H_2O)_{4-x}Cl_x^{2-x}(a) + nH_2A_{(0)} \leftrightarrow PdCl_y(HA)_m(H_2A)_{n-m}^{2-y-m}{}_{(0)} + mH^+{}_{(a)} + (x-y)Cl^-{}_{(a)} + (4-x)H_2O \tag{2}$$

Calculation of K_{ex} values from the intercept of each line using equation (3) showed that its value is fairly constant in each extraction system:

$$\log K_{ex} = \log D - pH - \log[Cl] - \log[H_2A] \tag{3}$$

$K_{ex} = 8 \pm 1$ in chloroform solution of H_2A from HNO_3 medium and $K_{ex} = 21 \pm 2$ in toluene solution of H_2A from HNO_3 medium.

The extracted complex has been confirmed by chemical analysis, thermoanalyses and IR spectroscopy. It was found that palladium is extracted according to the following extraction reaction:

$$Pd(H_2O)_2Cl_{2(a)} + H_2A_{(0)} = Pd(HA)CI_{(O)} + H^+_{(a)} + Cl^-_{(a)} + 2H_2O(4) \tag{4}$$

The value of ΔH obtained from the plot using a least squares fit is $-29.3\,kJ\,mol^{-1}$. Thus, extraction of palladium with H_2A is exothermic. The standard free energy of extraction was calculated from $\Delta G^\circ = -RT\log D$ as $\Delta G^\circ = -990\,J\,mol^{-1}$. The separation of Pd (II) from mixed solution of Pd(II)–Pt(IV) was achieved by adjusting the pH [43].

Tetradentate dianionic phenolic di-Schiff bases, such as H_2salen and its analogs, are well known as ligands that are easy to synthesize and have structural rigidity. They are used as selective extraction reagents for several kinds of metal cations [44–49]. Also the nitro-substituted analog of H_2salen for mutual separation of lanthanides was studied [50, 51].

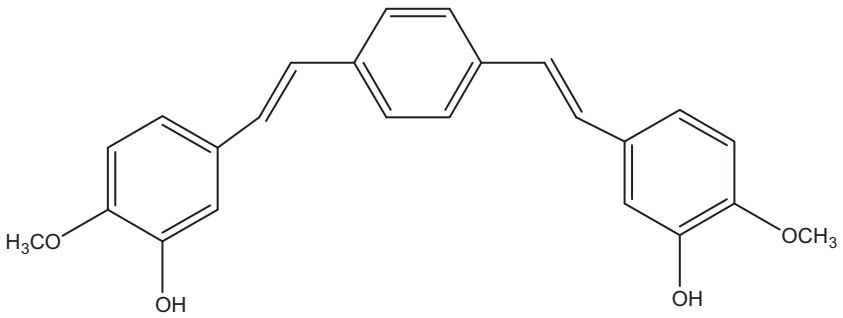
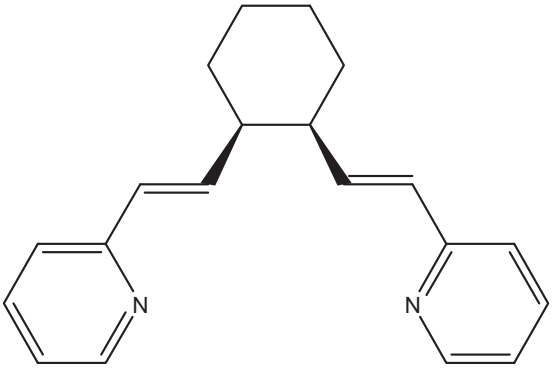
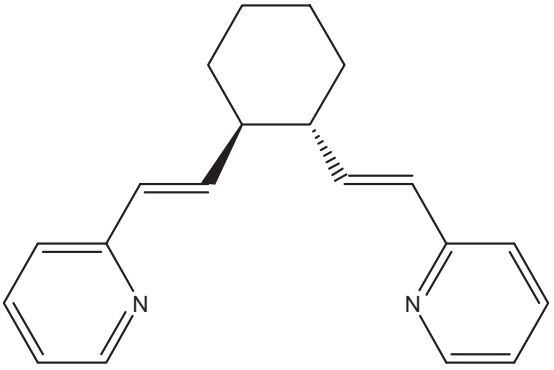


Figure 3. Structure of Schiff base.

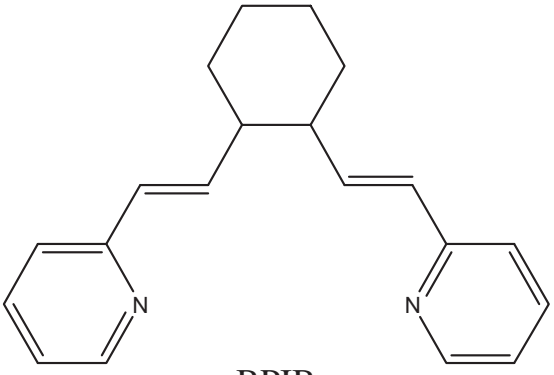
Downloaded by [Renmin University of China] at 10:48 13 October 2013



cis-BPIC



trans-BPIC

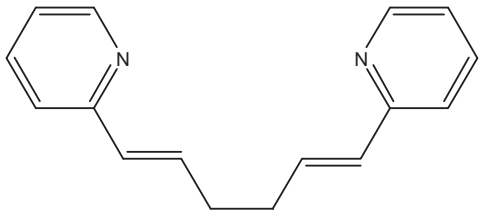


BPIB

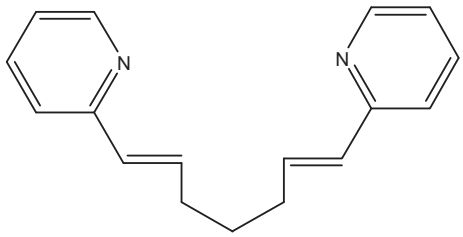
Figure 4. Chemical structure of cis-BPIC, trans-BPIC and BPIB.

The rigid structure of H_2salen is favorable for formation of 1 : 1 square-planar complex. Combination of this rigid structure and $>N^-$ donors has possible development of novel extraction reagent having specific selectivity.

Downloaded by [Renmin University of China] at 10:48 13 October 2013



N,N'-bis(2-pyridylmethylidene)-1,2-diiminoethane (L1)



N,N'-bis(2-pyridylmethylidene)-1,2-diiminopropane (L2)

Figure 5. Chemical structure of the studied Schiff base extraction.

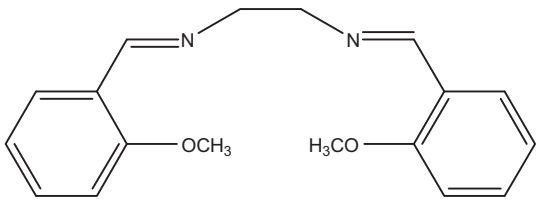


Figure 6. Structure of Schiff base bis(2-methoxybenzaldehyde)ethylene diimine.

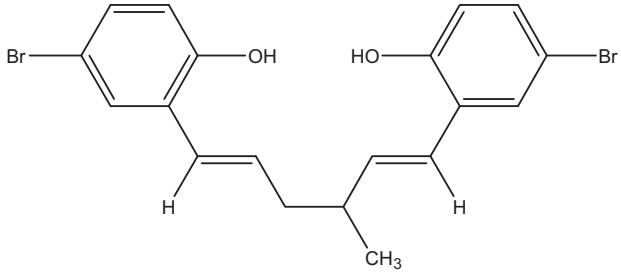
Naoki Hirayama *et al.* reported investigation of the nature of sulfonamide-type di-Schiff bases (figure 2), such as *N*,*N*′-bis[phenyl[o-(p-toluene sulfonamido)phenyl]methylidene]ethylene di-amine (H_2tsben-Ph_2) and its analogs, as chelate extraction reagents for divalent metal cations such as Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) including comparison with respective phenol type salens. These sulfonamide ligands are dianionic-quadridentate ones to form 1 : 1 complexes with divalent cations, confirmed from numerical analysis of relationship between distribution ratio of the metals and pH or ligand concentration. Furthermore, they showed extraction selectivity with Ni(II) suppressed and Zn(II) enhanced, originating mainly from use of sulfonamide-donors on complexation. This was remarkable on H_2tsben-Ph_2 ($\log K_{ex} = -10.57 \pm 0.11$ for Zn(II)), and may be controlled by structural rigidity of the ligands including delocalization of the π-conjugation including the sulfonamide-donor [52].

Wail Al Zoubi and coworkers studied separation of Cu(II) and Cr(III) from aqueous solution with solvent extraction using [*N*,*N*′-p-phenylene bis(5-amino-2-methyoxy-phenol)] (figure 3) as the extractant. The Schiff base was synthesized by reaction of terephthaldialdehyde and 5-amino-2-methoxy-phenol. The Schiff base has been studied by liquid–liquid extraction towards UO_2(II), Hg(II), Cu(II) and Cr(III) from aqueous phase to organic phase. Extraction efficiency for metals is in the order Cu(II) > Cr(III); UO_2(II) and Hg(II) are not extracted by Schiff base ($E < 1\%$) [53].

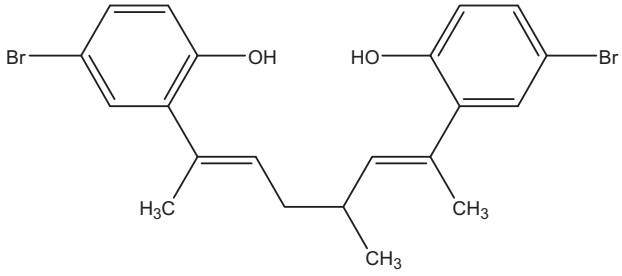
Downloaded by [Renmin University of China] at 10:48 13 October 2013

Di-Schiff base, *N*,*N*′-bis(2-pyridylmethylidene)-trans-1,2-diimin ocyclohexane (trans-BPIC), having sufficient hydrophobicity, is a neutral bidentate ligand in ion-pair extraction of divalent metal cations into nitrobenzene with picrate. The effect of steric restriction by structure around imine-N donors in trans-BPIC analogs on complexation with divalent metal cations in ion-pair extraction was investigated using *N*,*N*′-bis(2-pyridylmethylidene)-cis-1,2-diiminocyclohexane (cis-BPIC) and *N*,*N*′-bis(2-pyridylmethylidene)-o-diiminobenzene (BPIB) (figure 4). The former was used to observe the effect of geometrical restriction and the latter conjugate restriction. In BPIB-NaPic system, higher extractability was obtained than those in cis- and trans-BPIC systems, from increase of steric distortion from conformational restriction. Thus, extractability can be controlled by steric restriction on complexation [54].

Zahra synthesized two N4-type Schiff bases (figure 5), *N*,*N*′-bis(2-pyridylmethylidene)-1,2-diiminoethane (L1) and *N*,*N*′-bis(2-pyridylmethylidene)-1,3-diiminopropane (L2) by reaction of pyridine-2-carbaldehyde with ethylenediamine and propylenediamine, respectively. The binding abilities of L1 and L2 in dichloromethane towards Cu(II), Cd(II), Co (II), Ni(II), Zn(II) and Pb(II) ions were evaluated by performing competitive extraction experiments on mixtures containing these ions from aqueous picrate and nitrate media as a function of aqueous phase pH. The results show a pronounced selectivity of the ligands towards copper and cadmium. The copper/cadmium selectivity of the ligands is influenced by the nature of anions accompanying the extracted complexes. The ligands are more efficient complexing agents for cadmium in the presence of nitrate and acetate, whereas selectivity changes towards copper in the presence of picrate, perchlorate and thiocyanate [55].



N,N'-bis(2-hydroxyacetophenone)-1,2-propanediimine (L1)



N,N'-bis(5-bromo-2-hydroxybenzaldehyde)-1,2-propanediimine (L2)

Figure 7. *N*,*N*′-bis(2-hydroxyacetophenone)-1,2-propanedimine (L1) and *N*,*N*′-bis(5-bromo-2-hydroxybenzaldehyde)-1,2-propanedimine (L2).

Downloaded by [Renmin University of China] at 10:48 13 October 2013

Downloaded by [Renmin University of China] at 10:48 13 October 2013

Parmar *et al.* reported synthesis and characterization of copper(II) chelates of Schiff bases (H_2L), obtained by condensation of 4-butyryl-3-methyl-1-phenyl-pyrazoline-5-one (HBMPP) with o-phenylene diamine (H_2L^1) and p-phenylene diamine (H_2L^2). The extractability of copper(II) with H_2L in chloroform was examined. Effective extraction was observed with 1×10^{-3} mol dm^{-3} of ligands at pH 6.5 using H_2L^1 and pH 7.0 using H_2L^2 [56].

The liquid–liquid extraction of copper(II) with Schiff bases in chloroform from sulfate media is studied for pH and concentration of the extractant. Stoichiometry coefficients of the extracted species were determined by the slope analysis method. With salicylideneaniline, copper(II) is extracted as a mixed chelate complex, CuL_2HL. In the presence of substituent, the copper is extracted as simple chelates, CuL_2. The trends in the values of extraction constants were explained in terms of the nature of the substituents [57].

A method was developed for speciation of chromium in natural water samples based on homogeneous liquid–liquid extraction and determination by flame atomic absorption spectrometry (FAAS). In this method, Cr(III) reacts with the Schiff base (figure 6) to form a hydrophobic complex, which is subsequently entrapped in the sediment phase, whereas Cr (VI) remained in aqueous phase. The Cr(VI) assay is based on its reduction to Cr(III) by addition of sodium sulfite to the sample solution. Thus, separation of Cr(III) and Cr(VI) could be realized. Homogeneous liquid–liquid extraction based on pH-independent phase-separation was investigated using a ternary solvent system (water-tetrabutylammonium (TB^{A+})-chloroform) for preconcentration of chromium. The phase separation occurred by an ion-pair formation of TBA and perchlorate. Then sedimented phase was separated using a 100 μL micro-syringe and diluted to 1.0 mL with ethanol. The sample was introduced into the flame by conventional aspiration. After optimization of complexation and extraction conditions such as pH = 9.5, [ligand] = 1.0×10^{-4} M, [TBA^+] = 2.0×10^{-2} M, [$CHCl_3$] = 100.0 μL and [ClO_4^-] = 2.0×10^{-2} M, a preconcentration factor (Va/Vs) of 100 was obtained for only 10 mL of the sample. The relative standard deviation was 2.8% ($n = 10$). The limit of detection was sufficiently low at ppb level. The proposed method was applied for extraction and determination of chromium in natural water samples with satisfactory results [58].

Fathi *et al.* reported the synthesis of two new N_2O_2-type Schiff base extractants, *N*,*N*′-bis (2-hydroxyacetophenone)-1,2-propanediimine (L1) and *N*,*N*′-bis(5-bromo-2-hydroxybenzaldehyde)-1,2-propanediimine (L2) (figure 7), by reaction of corresponding ketone and aldehyde (2-hydroxyacetophenone and 5-bromo-2-hydroxybenzaldehyde, respectively) and 1,2-diaminopropane in ethanol. Distribution of the prepared ligands between sodium chloride aqueous phase and dichloromethane shows their suitability for solvent extraction.

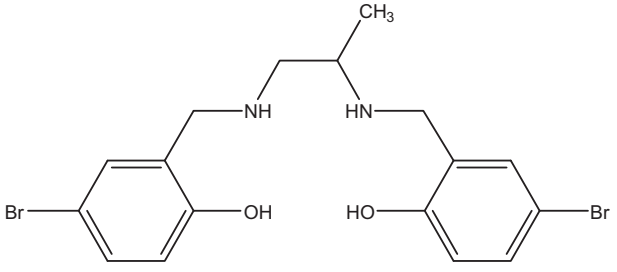


Figure 8. Structure of *N*,*N*′-bis(2-hydroxy-5-bromo-benzyl)-1,2-diaminopropane.

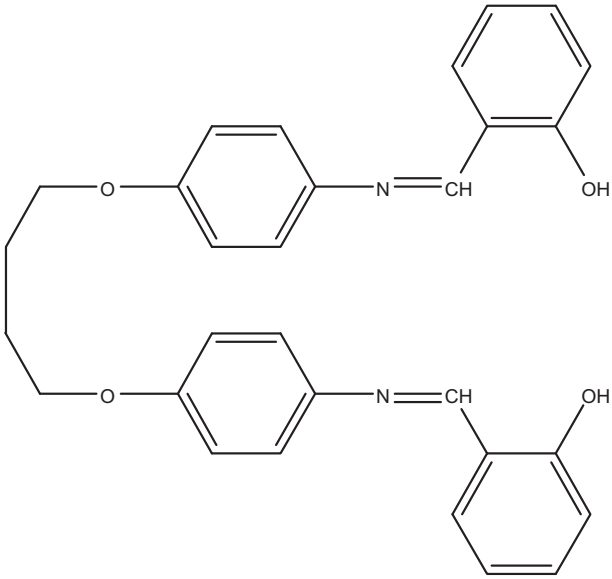


Figure 9. *N*,*N*′-bis(salicylaldehydene)-1,4-bis(paminophenoxy)butane (H_2L).

Liquid–liquid extraction experiments were performed for illustrating extractive performance of L1 and L2 towards copper(II). Both ligands transfer copper ions into the dichloromethane phase by a cation exchange mechanism. Analysis of the extraction data reveals that Cu (II) is extracted as complexes with a 1 : 1 metal to ligand ratio by both extractants. The ability of the studied Schiff bases for separation of copper from mixture with other normally associated metal ions was demonstrated by performing competitive extraction experiments of copper ions from solutions containing Pb(II), Zn(II), Ni(II), Cd(II) and Co(II) [59].

A combination of solvent extraction with spectrophotometric analysis is found in cases for which the latter is performed on the extracting phase. This is also the first instance in which solvent extraction was used in spectrophotometry or, in fact, in chemical analysis in general. Numerous metal ions are extractable by a solution of dithizone in chloroform or in carbon tetrachloride. Organic solutions are obtained in which the metal dithizonate complexes can be determined by spectrophotometry at different wavelengths. Many extractants such as acetyl acetone, 8-hydroxy quinoline, dimethyl glyoxime, cupferron, dithizone and sodium diethyl dithiocarbamate are used for spectrophotometric determination of copper [60].

Preconcentration and separation with solvent extraction of Cu(II) from aqueous solution using *N*,*N*′-bis(2-hydroxy-5-bromo-benzyl)1,2-diaminopropane (H_2L) were reported (figure 8). Separation of Cu(II) from Cd(II), Ni(II), Zn(II), Pb(II), Cr(III), Co(II) and Mn

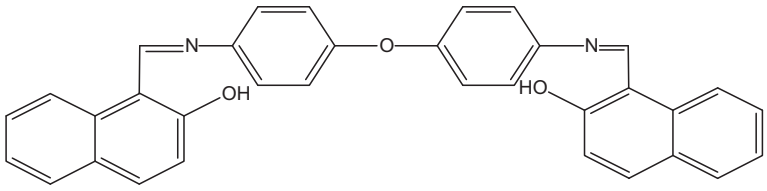


Figure 10. Structure of HAPMN.

Downloaded by [Renmin University of China] at 10:48 13 October 2013

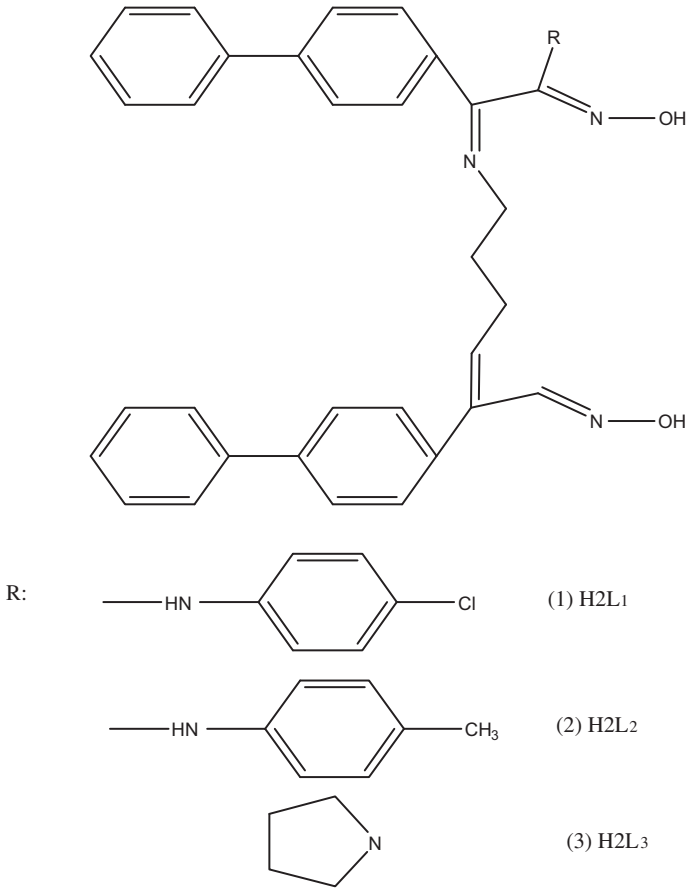


Figure 11. Synthetic route for the synthesis of ligands (H_2L^1, H_2L^2 and H_2L^3).

(II) in aqueous solutions at various pH values with H_2L has been described. The separation of Cu(II) could be accomplished quantitatively from other metal ions except Fe(III) at pH 3.5. Copper extraction was quantitative within the pH range of 3.5–10. Also the extraction efficiency decreases with increase in ionic strength of aqueous medium. The work shows the effect of A/O on percentage extraction which was satisfied by equation (9),

$$E\% = \frac{D}{D + A/O} \times 100 \tag{5}$$

where D is the distribution ratio, A and O are the volumes of the aqueous and organic phase, respectively. Equation (9) indicates that the extraction efficiency decreases with increasing A/O ratio. The influence of temperature on extraction of copper(II) by H_2L was studied using 1×10^{-3} M Cu(II) and 1×10^{-3} M ligand. Results showed a slight decrease in copper extraction as the temperature increased. From quantitative evaluation of the extraction equilibrium data, it has been deduced that the complex extracted is the simple 1 : 1 chelate, CuL. The extraction constant has a value of $\log K_{ex} = -4.05 \pm 0.04$ [61].

Downloaded by [Renmin University of China] at 10:48 13 October 2013

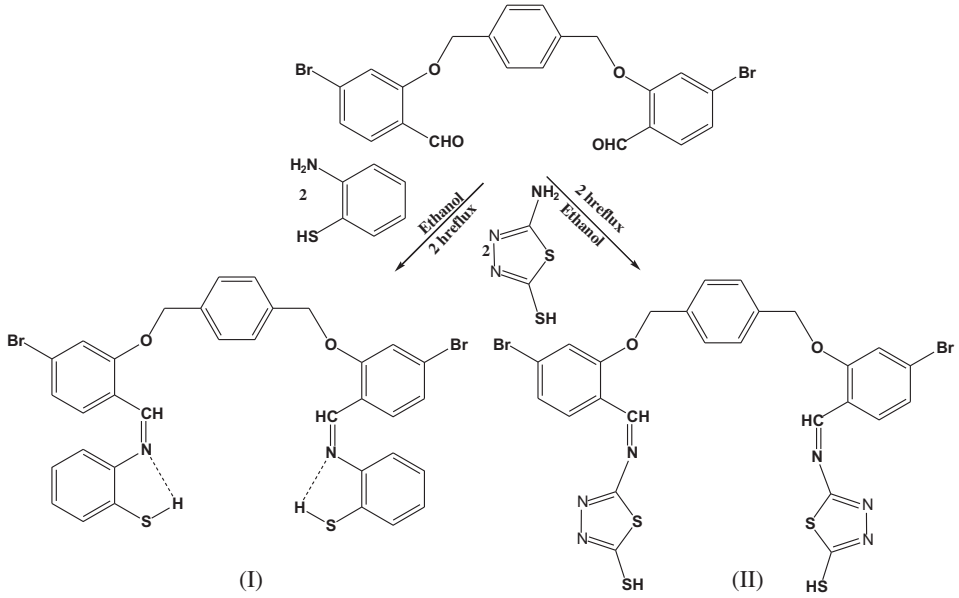


Figure 12. Structure of Schiff bases.

Separation with solvent extraction of Cu(II), Co(II) and Ni(II) from aqueous solution using *N*,*N*′-bis(salicylaldehydene)-1,4-bis(paminophenoxy)butane (H_2L) (figure 9) as the new extractant has been studied. The extractability and selectivity of divalent cations was evaluated as a function of relationship between distribution ratios of the metal and pH or ligand concentration. Cu(II) showed the highest extractability and selectivity at pH 7.8, whereas Ni(II) and Co(II) were best at pH 9.2. From quantitative evaluation of the extraction equilibrium data, it has been deduced that the complexes extracted are the simple 1 : 1 chelates, CuL, CoL and NiL [62].

A fundamental study was developed concerning solvent extraction of tetravalent metal ions, zirconium(IV), hafnium(IV) and thorium(IV). Their extraction behavior in toluene was investigated with a naphthol-derivative Schiff base, 1-({[4-(4-{[(E)-1-(2-hydroxy-1-naphthyl)methyliden]-amino}phenoxy)phenyl]imino}methyl)-2-naphthol (HAPMN) (figure 10). Spectrophotometrical examination of complex formation between HAPMN and Zr (IV), Hf(IV) and Th(IV) in acetonitrile revealed the formation of stable 1 : 1 complexes in solution. After thorium extraction in toluene, $[Th(OH)_3HA]$ was formed. For zirconium and hafnium extraction adduct was $[M_4(OH)_8(H_2O)_{16}Cl_6 2HA]$. The stoichiometric coefficients of these extracted species were determined by the slope analysis method. The extraction reaction followed a cation exchange mechanism [63].

Dede and coworkers reported synthesis of twelve homo- and hetero-nuclear copper(II) complexes of tetradentate Schiff base ligands (figure 11) containing N_4 donor sets by employing several steps. The extraction ability of the ligands has been examined by liquid–liquid extraction of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Pb(II), Cd(II) and Hg(II). The ligands show strong binding toward copper(II). The homo- and hetero-nuclear copper (II) complexes were each tested for their ability to catalyze disproportionation of hydrogen peroxide in the presence of added imidazole [64].

Downloaded by [Renmin University of China] at 10:48 13 October 2013

Downloaded by [Renmin University of China] at 10:48 13 October 2013

Kanttekin and others reported the use of $N_2O_2S_2$ Schiff base containing aromatic moieties for the transfer of various metal ions from aqueous phase into the organic phase in liquid–liquid extraction [65–67].

Schiff bases (figure 12) containing nitrogen, sulfur and oxygen donors were synthesized in a multi-step reaction sequence. The Schiff base (I) was used in solvent extraction of metal chlorides, such as Cu(II) from aqueous phase to the organic phase. Influence of pH, solvent, ionic strength of aqueous phase, aqueous to organic phase, and concentration of the extractant were investigated for extractability of metal ions. The effect of chloroform, dichloromethane, and nitrobenzene as solvents over the metal chlorides extraction was investigated at 25 ± 0.1 °C by using flame atomic absorption and the ability of extraction in solvents was $C_6H_5NO_2 > CHCl_3 > CH_2Cl_2$ [68].

The competitive solvent extractions of alkali metals by nano-baskets of di-ionizable calix[4]arenes were studied using nine scaffolds and 34 calix[4]arene derivatives. The objective of this work was to assess the effect of changing the pendant groups as well as variation of macrocycle conformation, orientation, and position of pendant moieties upon the extraction efficiency, selectivity, and pH of calix[4]arene complexes. Alkali metal cations were extracted from aqueous solutions into chloroform by di-ionizable calix[4]arene derivatives and were measured using ion chromatography. The results revealed that alternation of aryl group in the pendant moieties, changing their orientation from cis- to trans- as well as ortho- to para-analogs, revealed no changes in the selectivity, extraction efficiency and pH of calix[4]arene complexes. Alternation of ring conformation (cone, 1,2-alternate, and partial-cone) showed a pronounced influence upon complexation of alkali metal cations [69].

Recent reports have indicated that Trivalent Actinide–Lanthanide Separation by Phosphorus reagent Extraction from Aqueous Komplexes (TALSPEAK)-type separations chemistry can be improved through the replacement of bis-2-ethyl(hexyl) phosphoric acid (HDEHP) and diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic acid (DTPA) with the weaker reagents 2-ethyl(hexyl) phosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) and *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetic acid (HEDTA), respectively. This modified TALSPEAK has been provided with an adjusted acronym of TALSQuEAK (Trivalent Actinide–Lanthanide Separation using Quicker Extractants and Aqueous Komplexes). Among several benefits, TALSQuEAK chemistry provides more rapid phase transfer kinetics, is less reliant on carboxylic acids to mediate lanthanide extraction, and allows a simplified thermodynamic description of the separations process that generally requires only parameters available in the literature to describe metal transfer. This article focuses on the role of carboxylic acids in aqueous ternary (M-HEDTA-carboxylate) complexes, americium/lanthanide separations, and extraction kinetics. Spectrophotometry (UV–vis) of the Nd^{3+} hypersensitive band indicates the presence of aqueous ternary Nd–Lac–HEDTA species (Lac = lactate, K 111 = 1.83 ± 0.01 at $1.0\,\mathrm{mol\,L^{-1}}$ ionic strength, Nd(HEDTA) $+Lac^- \leftrightarrow$ Nd(HEDTA)Lac^-). While lower levels ($0.1\,\mathrm{mol\,L^{-1}}$ vs. $1.0\,\mathrm{mol\,L^{-1}}$) of carboxylic acid are still necessary to control pH and encourage phase transfer of the heavier lanthanides, application of different carboxylic acids does not have an overwhelming impact on Ln/Am separations or extraction kinetics relative to conventional TALSPEAK separations. TALSQuEAK separations come to equilibrium in two to five minutes depending on the system pH using only $0.1\,\mathrm{mol\,L^{-1}}$ total lactate or citrate [70].

The formation of ternary complexes between lanthanide ions [Nd(III) or Eu(III)], octyl (phenyl)-*N*,*N*-diisobutyl-carbamoylmethylphosphine oxide (CMPO), and bis-(2-ethylhexyl) phosphoric acid (HDEHP) was probed by liquid–liquid extraction and spectroscopic tech-

niques. Equilibrium modeling of data for the extraction of Nd(III) or Eu(III) from lactic acid media into *n*-dodecane solutions of CMPO and HDEHP indicates the predominant extracted species are $[Ln(AHA)_2(A)]$ and $[Ln(CMPO)(AHA)_2(A)]$, where Ln = Nd or Eu and A represents $DEHP^-$. FTIR (for both Eu and Nd) and visible spectrophotometry (in the case of Nd) indicate the formation of $[Ln(CMPO)(A)_3]$ when CMPO is added to *n*-dodecane solutions of LnA_3 compounds. Both techniques indicate a stronger propensity of CMPO to complex Nd(III) vs. Eu(III) [71].

The coordination chemistry and cationic binding properties of 2,6-bis(pyrazol-1-ylmethyl)pyridine (**L_1**), 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (**L_2**), and 2,6-bis(3,5-ditertbutylpyrazol-1-ylmethyl)pyridine (**L_3**) with zinc(II) and cadmium(II) have been investigated. Reactions of **L_2** with zinc(II) and cadmium(II) nitrate or chloride salts produced monometallic complexes $[Zn(NO_3)_2(\mathbf{L_2})]$ (**1**), $[ZnCl_2(\mathbf{L_2})]$ (**2**), $[Cd(NO_3)_2(\mathbf{L_2})]$ (**3**) and $[CdCl_2(\mathbf{L_2})]$ (**4**). Solid state structures of **1** and **3** confirmed that **L_2** binds tridentate. While the nitrates in **1** are monodentate, in cadmium complex (**3**), they are bidentate. **L_1**–**L_3** show binding efficiencies of 99% for zinc(II), 60% for lead(II), and 30% for cadmium (II) cations from aqueous solutions of the metal ions. Theoretical studies using Density Functional Theory were consistent with the observed extraction results [72].

Schiff bases are powerful extractants for metal ions. A major feature of theses extractants was high sensitivity for transition metal ions and structural rigidity. Schiff bases are readily synthesized from inexpensive starting materials. In contrast to a number of reports on liquid–liquid extraction of divalent metal ions with di- and macrocyclic Schiff bases, reports on extraction studies with bidentate mono-Schiff bases are limited. The synergic effect between mono-Schiff bases and other extractants has not been investigated. Therefore, four synergistic extraction systems for copper(II) separation from sulfate medium, by a mixture of chelating bidentate mono-Schiff base extractants, viz, *N*-salicylideneaniline (SA), *N*-(2-hydroxy-1-naphthalidene)aniline (HNA), *N*-salicylidene-1-naphthylamine (SN), and *N*-(2-hydroxy-1-naphthalidene)-1-naphthylamine (HNN), with acyclic ayclic polyether non-ionic surfactant (Lutensol A7 N) were examined (see figure 13) [73–92].

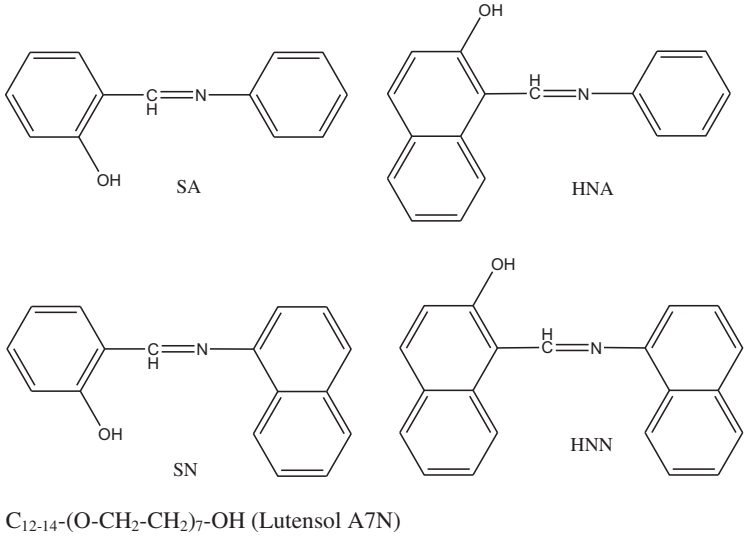


Figure 13. Chemical structures of bidentate mono-Schiff base extractants and non-ionic surfactant used.

Downloaded by [Renmin University of China] at 10:48 13 October 2013

Liquid–liquid extraction of copper(II) with bidentate mono-Schiff base extractants (HL), SA, HNA, SN, and HNN, from a weakly acidic sulfate media into chloroform was studied in both the absence and presence of acyclic polyether non-ionic surfactant (S). In the absence of the non-ionic surfactant, the extractability of copper(II) was 92.6% with SA, 89% with HNA, 81% with SN, and 80% with HNN. The estimated extraction constants (log K_{ex}) of the four extractants revealed that the extraction efficiency increased in the order HNN < SN < HNA < SA. Copper(II) was extracted as CuL_2 (HL) with SA and HNA, and as CuL_2 with SN and HNN. The extraction of copper(II) was significantly enhanced with HL into chloroform upon addition of a non-ionic surfactant, with extractability of 100% reached. The stoichiometry of the extracted complexes was CuL_2S. The synergic extraction ability of extractants changed, SA > HNA > SN∼HNN, whereas the synergic effect was HNN > SN > HNA∼SA [93].

An advantage of solvent extraction is that both separation and preconcentration, which are often required, can be obtained in the same step [94, 95]. The first instance of chemical analysis of metal ions was combination of liquid extraction and spectrophotometric methods, in which the analysis was performed on the extracting phase. Nevertheless, the solvent extraction of nickel is still an important process and is used in several plants to recover and separate nickel from wastewaters [96, 97]. Ligands such as dimethylglyoxime, dithizone, and sodium-diethyldithiocarbamate are extractants for extraction/spectrophotometric determination of nickel [98].

An extraction-spectrophotometric method for determination of nickel at sub ppm level using 2-[(2-mercaptophenylimino)methyl]phenol (MPMP) (figure 14) as the new extractant was described. The reagent reacts with nickel(II) at pH > 10 forming a 1 : 2 brown complex, which is extracted into chloroform. The complex has a maximum absorption at 421 nm with the molar absorptivity of $2.41 \times 10^5\,M^{-1}\,cm^{-1}$. Beer's law is obeyed from 0.011–0.30 $\mu g\,mL^{-1}$. Sandell's sensitivity for 0.001 absorbance unit is $5.34 \times 10^{-4}\,\mu g\,cm^{-2}$. The relative standard deviation at 0.018 $\mu g\,mL^{-1}$ is 1.1% ($n = 8$). The procedure was applied to determination of nickel in wastewater and standard alloy and the accuracy was determined by recovery experiment, independent analysis by furnace-AAS, and analysis of a certified reference material [99].

Liquid–liquid extraction of copper(II) with Schiff bases in chloroform from sulfate media was studied for pH and concentration of the extractant. Stoichiometry coefficients of the extracted species were determined by the slope analysis method. With salicylideneaniline, copper(II) was extracted as a mixed chelate complex, CuL2HL. In the presence of substituent, the copper is extracted as simple chelates, CuL2. The trends in the values of extraction constants were explained in terms of the nature of the substituents [100].

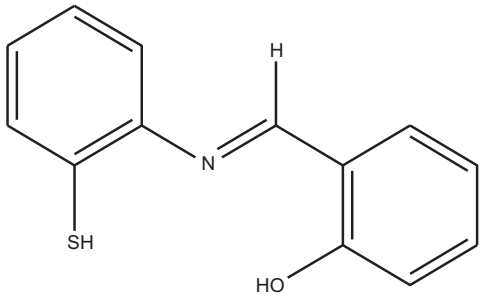


Figure 14. Structure of the Schiff base.

Downloaded by [Renmin University of China] at 10:48 13 October 2013

3.2. *Macrocyclic and acyclic ligands*

Acyclic and macrocyclic Schiff bases (figure 15) containing phenol groups showed good extraction for bivalent transition metals, following an Irving-Williams series. Acyclic and macrocyclic Schiff bases containing phenol and thiophene were synthesized and the effect of ligand on the extraction of metal ions was studied. Phenols in the Schiff base led to a large increase in the percent extraction of manganese(II) and iron(III) classified as "hard" metal ions. Compared with a macrocyclic Schiff base, the corresponding acyclic counterpart had reasonable reactivity toward metal ions and better solubility in organic solvents. The substitution of methoxy groups for phenolic OH resulted in a marked decrease in the extractability of manganese(II) and iron(III). Thiophene groups in the Schiff base increased extractability of silver(I), palladium(II) and platinum(II) classified as "soft" metal ions. Cobalt(II), nickel(II), copper(II) and zinc(II) were quantitatively extracted by nitrogens of amine in the Schiff base. Substitution of oxygen for amine resulted in a marked decrease in the extractability of cobalt(II), nickel(II), copper(II) and zinc(II) [101].

A series of acyclic pyrazole compounds containing one, two, three or four pyrazole rings were prepared and demonstrated to extract only transition metal cations [102–105]

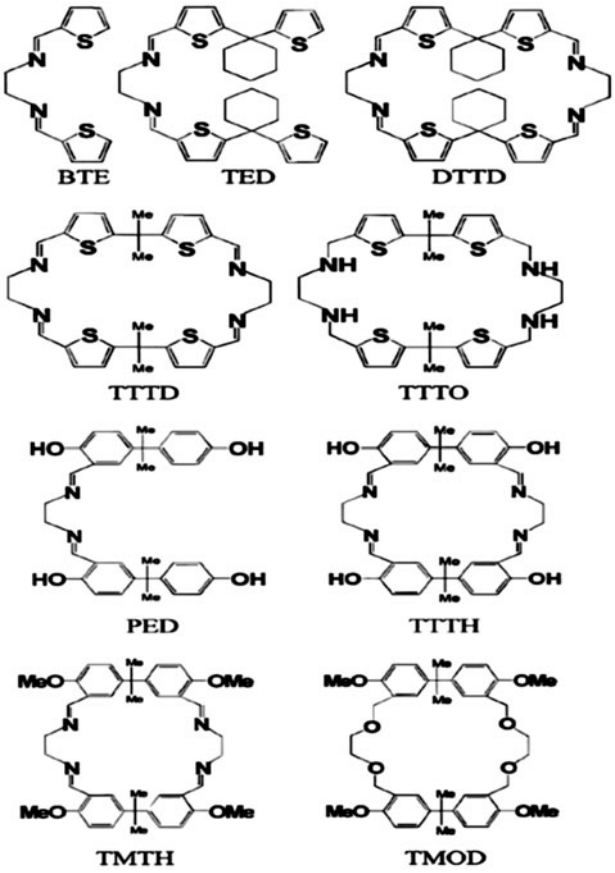


Figure 15. Acyclic and macrocyclic Schiff bases containing phenol and thiophene groups.

Downloaded by [Renmin University of China] at 10:48 13 October 2013

whereas macrocyclic pyrazolic compounds are expected to also form stable complexes with alkali metals [106, 107].

The synthesis of a new tetrapyrazolic macrocycle (figure 16) with a functionalized arm is described. The complexing properties of this new compound towards alkali metal ions (K(I), Na(I), Li(I)) were studied by liquid–liquid extraction and liquid membrane transport processes [108].

In this work metal picrates were extracted into the organic phase by complex formation with the macrocycle; the decrease in absorbance of the picrate in the aqueous phase was followed by UV spectroscopy. The percentage limits of extraction are given in table 1.

In order to show that the macrocycle does not simply protonate in the presence of metal picrates, the authors have determined the extracted cation percentage by atomic absorption measurements and the same results were found.

The results in table 1 show that in analogy to previous work in which acyclic pyrazolic compound A with a weak affinity for alkali cations led to no extraction properties and

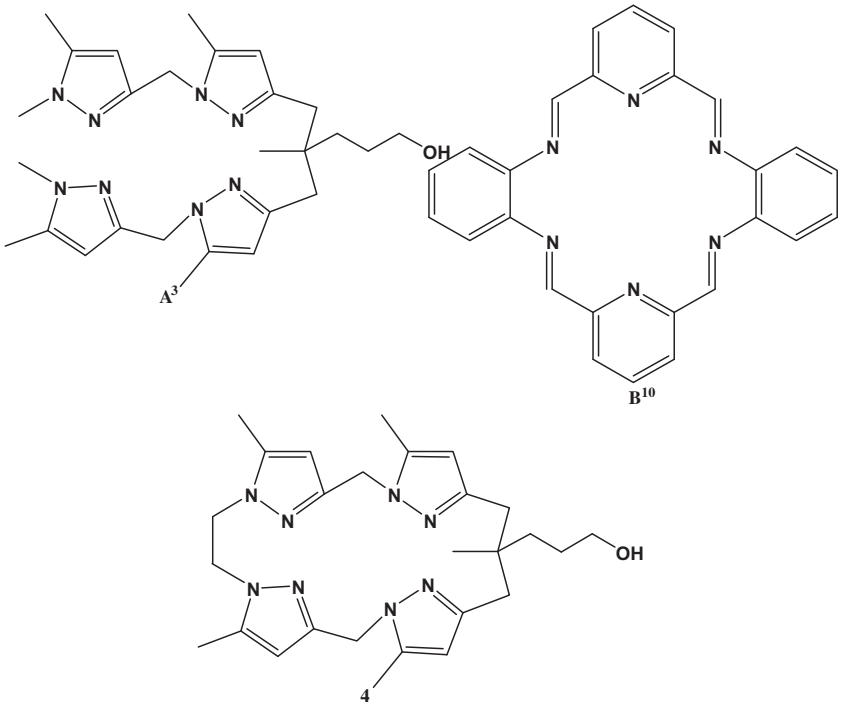


Figure 16. New tetrapyrazolic macrocycle 4 and literature compounds A and B.

Table 1. Yields of extraction of alkali metal ions.

Potassium (1.33 A°)		Sodium (0.98 A°)	Lithium (0.60 A°)
4	50	38	38
A	0	0	0
B	0	0	0

Notes: A: acyclic pyrazolic compound.
B: marcocycle with pyridine-type sp^2 nitrogens.

Downloaded by [Renmin University of China] at 10:48 13 October 2013

pyrazolic macrocycles were expected to form stable complexes, again this new macrocycle shows better extraction percentages for alkali cations.

We noticed a high affinity for all alkali metal cations, especially for potassium. This is related to the size of the cavity, which is possibly enlarged at the junctions between pyrazole units. The ionic radii and the flexibility of the macrocycle also enable cation binding with a possible contribution from the side arm. The complexing power of this pyrazolic macrocycle was attributed to the existence of sp^2 lone pairs forming an electronegative internal cavity [108].

Three new macrocyclic Schiff bases: (II, IV and VI) (figure 17) containing nitrogen-oxygen donors were synthesized by reaction of 1,4-bis(2-formylphenyl)-1,4-dioxabutane(I) 1,4-bis(2-formylphenyl)-1,4,7-trioxaheptane(III) and 1,10-bis(2-formylphenyl)-1,4,7,10-tetraoxadecane(V) with oxydianiline. Liquid–liquid extraction of metal picrates such as Ag (I), Cu(II) and Ni(II) from aqueous phase to organic phase was carried out using these ligands. The composition of extracted Ag(I) complex was (2 : 1) (L : M) and Cu(II) complex was (1 : 1) (L : M) for VI [109].

Two new macrocyclic hydrazone Schiff bases (figure 18) were synthesized by reaction of succindihydrazide and adipdihydrazide with acetylacetone. Hydrazones have been studied for liquid–liquid extraction towards s-metal ions (Li(I), Na(I), and K(I)) and d-metals

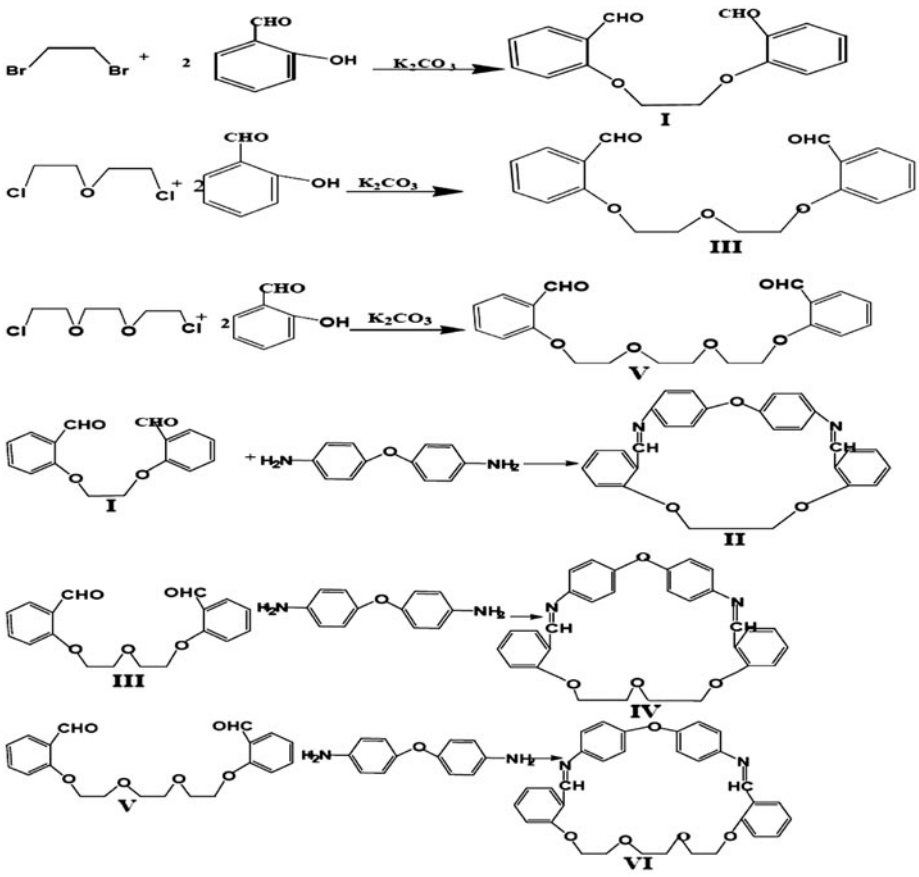


Figure 17. Scheme of synthesis of Schiff bases.

Downloaded by [Renmin University of China] at 10:48 13 October 2013

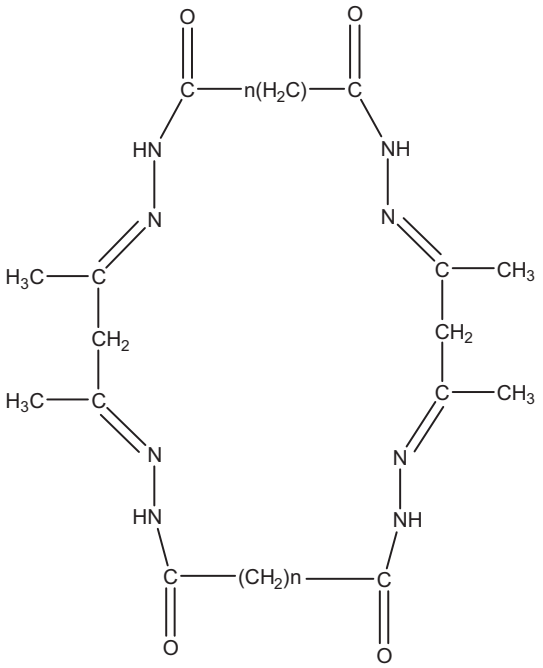


Figure 18. Structure of macrocyclic hydrazone Schiff bases ($n = 2$, 4).

(Cu(II) and Cr(III)) from aqueous phase to organic phase. The effect of chloroform and dichloromethane as organic solvents over the metal chloride extraction was investigated at 25 ± 0.1 °C by using flame atomic absorption with differences between the two solvents in extraction selectivity [110].

Macrocyclic hydrazone Schiff bases (figure 19) were synthesized by reaction of pyridine-2,6-dicarbohydrazide and pyridine-2,6-thiodicarbohydrazide with dicarbonyls. The Schiff base from pyridine-2,6-dicarbohydrazide and benzyl has been studied for liquid–liquid extraction towards Cu(II) and Cr(III) from aqueous phase to organic phase. The effect of chloroform and dichloromethane as organic solvents over the metal chloride extraction was investigated at 25 ± 0.1 °C by using flame atomic absorption. The extraction of Cu(II) and Cr(III) ions increased with increasing the pH of the aqueous medium and with the concentration of the polydentate Schiff base [111].

A new solvent extraction system using a hydrazone derivative 1,2-cyclohexanedione bis-benzoylhydrazone (1,2-CHBBH) has been studied to separate and quantify the different fractions of copper present in natural waters. The influence of different variables on the extraction has been studied, such as the type of organic solvent, the reagent concentrations in the extraction and back-extraction solutions, the sample pH and the extraction time. Under selected conditions, the influence of both organic and inorganic ligands present in natural waters on the efficiency of the extraction has been investigated. Thus, the effect of the major anion present (Cl^-, HCO_3^-, SO_4^{2-}, Br^-) as well as the effect of humic substances have been analyzed. Differences in the extraction efficiency were observed when organic ligands were presented in the samples. These differences allow the selective separation and quantification of the non-labile copper fraction in natural waters [112].

Downloaded by [Renmin University of China] at 10:48 13 October 2013

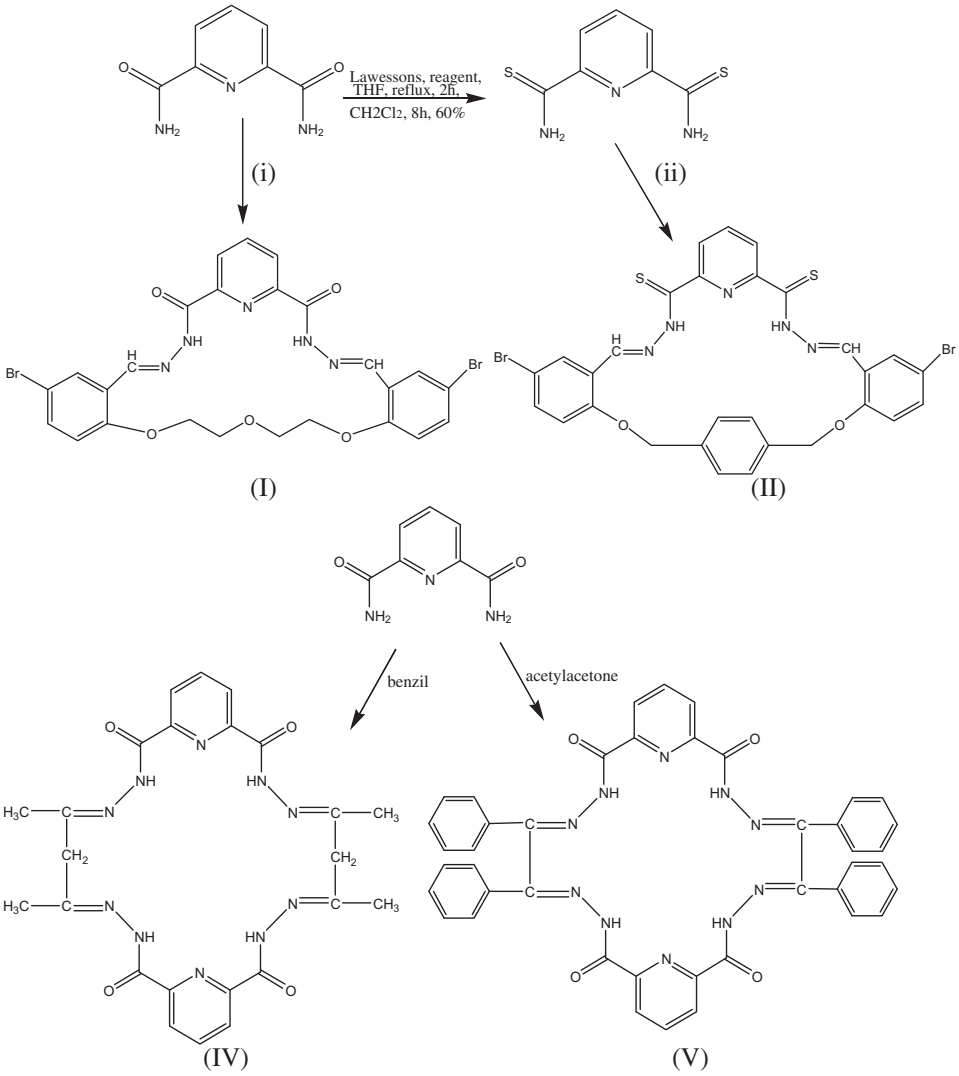


Figure 19. Structure of Schiff bases (I–V).

Twelve homo- and hetero-nuclear copper(II) complexes of tetradentate Schiff bases containing N(4) donor sets have been prepared by employing several steps. All copper(II) complexes are 1 : 2 electrolytes as shown by their molar conductivities in DMF and are paramagnetic. The subnormal magnetic moment values of the di- and tri-nuclear complexes indicated very strong anti-ferromagnetic interaction. The extraction ability of the ligands has been examined by liquid–liquid extraction of Mn(II), Co(II), Ni(II), Cu(II), Zn (II), Pb(II), Cd(II) and Hg(II). The ligands show strong binding ability toward copper(II) ion. Furthermore homo- and hetero-nuclear copper(II) complexes were each tested for their ability to catalyze disproportionation of hydrogen peroxide in the presence of imidazole [113].

Downloaded by [Renmin University of China] at 10:48 13 October 2013

Quantitative extraction of iron(III) and gallium(III) was investigated with the recently synthesized macrocyclic Schiff base containing bisphenol A subunits. The phenol groups in the Schiff base led to a large increase in the percent extraction of trivalent metal ions. The substitution of methoxy groups for phenolic OH ligands resulted in a marked decrease in the extractability of metal ions, and no iron(III) was extracted. The corresponding acyclic Schiff base had reasonable reactivity toward metal ions and better solubility in organic solvents. The iron (III) and gallium(III) complexes with macrocyclic and acyclic Schiff bases were quantitatively extracted into nitrobenzene without the presence of bulky counter anions. A single extraction gave a good separation of iron(III) from iron(II) in mole ratios 4 : 1 to 1 : 3. The red iron(III) complexes can be used for the extraction-spectrophotometric determination of iron(III). The apparent molar absorptivity at 518 nm is $5.43 \times 1031\,\mathrm{mol^{-1}\,cm^{-1}}$ [114].

Two types of macrocyclic Schiff bases containing either thiophene or phenol were synthesized and the effect of ligand on the liquid–liquid extraction of bivalent transition metal ions was studied. The phenol groups in the macrocycle led to a large increase in extraction of transition metal ions. The least stable manganese(II) complex was extracted quantitatively into nitrobenzene as an ion pair with tetraphenylborate at pH 9. Copper(II) was selectively extracted from weakly acidic media, permitting its separation from manganese (II), cobalt(II), nickel(II) and zinc(II). The composition of extracted copper(II) species was evaluated. The extractability of metal complexes with a cyclic tetraaza Schiff base has been compared with that of the corresponding acyclic Schiff base [115].

Acyclic and macrocyclic Schiff bases containing bisphenol A subunits were synthesized and the effect of ligand atoms on the liquid–liquid extraction of manganese(II), copper(II) and zinc(II) was studied. The phenol groups in the Schiff base led to a large increase in the percent extraction of transition metal ions. The substitution of methoxy groups for phenolic OH resulted in a marked decrease in the extractability of metal ions. Compared with a macrocyclic Schiff base, the corresponding acyclic counterpart had reasonable reactivity toward metal ions and better solubility in organic solvents. Copper(II) complexes with acyclic Schiff bases were quantitatively extracted into nitrobenzene without the presence of bulky counter anions. Mutual separation of zinc(II), copper(II) and manganese(II) can be achieved by proper selection of pH and extractant [116].

Liquid–liquid extraction of copper(II) with Schiff bases from salicylaldehyde and aniline and its derivatives in chloroform were studied. Slope analysis results were consistent with the extraction of copper(II) as $CuL_2(HL)$. Their extraction showed dependence on the position of substituent present on aniline [117].

Two new macrocyclic Schiff bases, (5) and (7), containing nitrogen-sulfur donors were synthesized by reaction of α,α^1-bis(o-aminophenylthio)-1,2-xylene with glyoxal and phthaldialdehyde (figure 20), respectively. The liquid–liquid extraction of metal picrates such as Ag(I), Hg(II), Cd(II), Zn(II), Cu(II), Ni(II), Mn(II), and Na(I) from aqueous phase to the organic phase was carried out using the ligands. The effect of chloroform and dichloromethane as organic solvents over the metal picrate extractions was investigated at 25 $\pm 0.1\,^{\circ}\mathrm{C}$ by using UV–visible spectrometry. The extractability and selectivity of the tested metal picrates were evaluated. The values of the extraction constants ($\log K_{ex}$) were determined for the extracted complexes [118].

Liquid–liquid extraction of uranium(VI) with the binary mixture of quadridentate Schiff base, bis-salicylidene ethylene diamine (H_2Salen) (H_2A) and neutral donors viz., triphenyl arsine oxide (TPAsO), triphenyl phosphine oxide (TPPO) and tri-n-octyl phosphine oxide (TOPO) has been studied. The extraction order in the pH range 2.5 to 5.5 is bis-salicylidene ethylene diamine < bis-salicylidene ethylene diamine + triphenyl

Downloaded by [Renmin University of China] at 10:48 13 October 2013

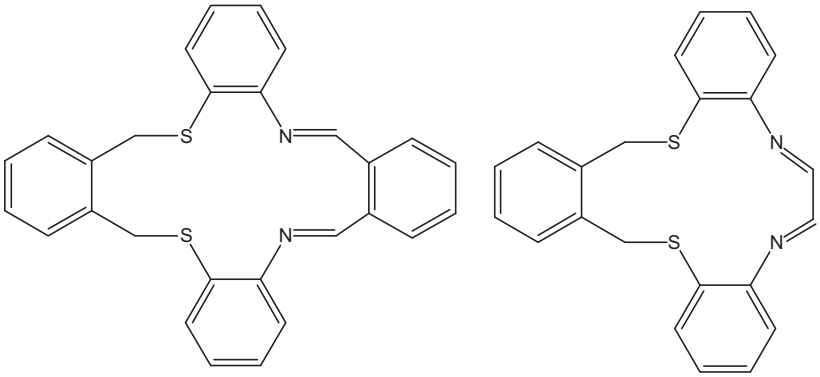


Figure 20. The synthesis pathways to the crown ethers (5 and 7) used in the literature study.

phosphine oxide < bis-salicylidene ethylene diamine + tri-n-octyl phosphine oxide < bis-salicylidene ethylene diamine + triphenyl arsine oxide. The composition of the extracted species derived from slope analysis are ($UO_2A \cdot 2TOPO$) and ($UO_2A \cdot 2TPPO$) [119].

Liquid–liquid extractions of zirconium/IV/, thorium/IV/ and uranium/VI/ with a tetradentate Schiff base, bis/salicylidene/ethylenediamine/H_2Salen/ in benzene as the diluent have been studied. Comparison of such results with those of a bidentate Schiff base, *N*-salicylidene-p-toluidine/HSalTol/ shows that the extraction of UO_2^{2+} is significantly improved if

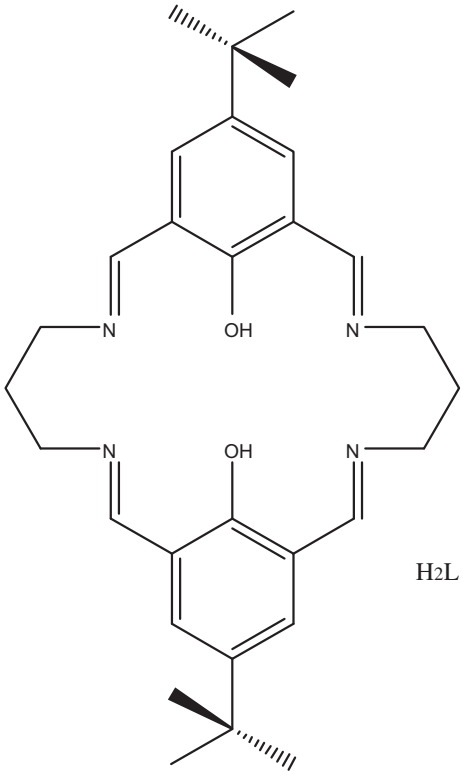


Figure 21. Structure of macrocyclic Schiff base.

Downloaded by [Renmin University of China] at 10:48 13 October 2013

H_2Salen is used instead of HSalTol. A single extraction at pH 6.5 with H_2Salen removes uranium/VI/. Extraction of all three metals becomes quantitative at pH 6.5. The extracted species, which have been derived from slope-analyses of extraction results, are $[Zr_4/OH/_{12}/HSalen/_2]Cl_2$, $[UO_2/OH//HSalen/]$ and $[Th/OH/_3/HSalen/]$ [49].

The Robson macrocycle has been extensively studied since reported in 1991 of its synthesis via the metal-templated Schiff-base condensation of 2,6-dialdehyde- or 2,6-diketophenol with an appropriate diamine (figure 21), and vast literature of complexation chemistry has been reported for these and related ligands. In the absence of a metal ion, however, the cyclized product is not isolated, although more recently the diprotonated salt $[H_4L]^{2+}$ has been prepared via cyclization of components under acidic conditions [120]. There is literature reported about the first synthesis and isolation of free H_2L and its use for selective and efficient extraction and transport of Cu(II).

4. Conclusions

Schiff bases have been widely explored for industrial applications. However, solvent extraction of this class of compounds deserves further investigation. This becomes clear when plant pathogens are considered. Although the research on this subject is incipient, a number of reports disclosing the effects of the Schiff bases on pathogens of clinical interest have been increasing. Schiff base compounds have been shown to be promising for design of more efficient chelates. Advances in this field will require analyses of the structure–activity relationships of the Schiff bases as well as the mechanism of action of these compounds.

The synthesis of new macrocyclic Schiff bases and their use as chelates will pave the way for applications of such solvent extraction for the removal of various metal ions from the natural water or wastewater.

We have reviewed Schiff bases, which have an unusual aptitude for formation of complexes with metal ions, demonstrating that these Schiff bases extract metal ions. Schiff bases are an excellent carrier for selective and efficient extraction of some metal ions. Such extraction of metal ions is important for heavy metal pollution control.

References

[1] H. Schiff. *Justus Liebigs Ann. Chem.*, **131**, 118 (1864).
[2] R.H. Holm, G.W. Everett, Jr., A. Chakravorty. *Inorg. Chem.*, **7**, 83 (1966).
[3] R. Atkins, G. Brewer, E. Kokot, G.M. Mockler, E. Sinn. *Inorg. Chem.*, **24**, 127 (1985).
[4] D.N. Dhar, C.L. Taploo. *J. Sci.*, **41**, 501 (1982).
[5] P. Przybylski, A. Huczynski, K. Pyta, B. Brzezinski, F. Bartl. *Curr. Org. Chem.*, **13**, 124 (2009).
[6] G. Bringmann, M. Dreyer, J.H. Faber, P.W. Dalsgaard, D. Staerk, J.W. Jaroszewski, C. Ancistrotanzanine. *J. Nat. Prod.*, **67**, 743 (2004).
[7] A.O. de Souza, F.C.S. Galetti, C.L. Silva, B. Bicalho, M.M. Parma, S.F. Fonseca. *Quim. Nova*, **30**, 1563 (2007).
[8] Z. Guo, R. Xing, S. Liu, Z. Zhong, X. Ji, L. Wang. *Carbohydr. Res.*, **342**, 1329 (2007).
[9] K.N. Campbell, H. Sommers, B.K. Campbell. *J. Am. Chem. Soc.*, **66**, 82 (1944).
[10] J. Hine, C.Y. Yeh. *J. Am. Chem. Soc.*, **86**, 2669 (1967).
[11] I.A. Savich, A.K. Pikaev, I.A. Lebedav, V.I. Spitsyn. *Vestnik. Moskov. Univ.*, **11**, 225 (1956).
[12] H. Tazoki, K. Miyano. *J. Chem. Soc.*, 9769 (1959).
[13] D.N. Robertson. *U.S.P.*, **2**, 101 (1960).
[14] C.M. Brewster. *J. Am. Chem. Soc.*, **46**, 2463 (1924).

Downloaded by [Renmin University of China] at 10:48 13 October 2013

[15] C. Munir, S.M. Yousaf, N. Ahmad. *J. Chem. Soc. Pak.*, **7**, 301 (1985).
[16] G.M. Loudon. *Organic Chemistry*. p. 874, 4th Edn, Addison-Wesley, California (2002).
[17] I.M. Kolthoff, E.B. Sandell. *J. Am. Chem. Soc.*, **63**, 1941 (1906).
[18] H. Irving, R.J.P. Williams. *J. Chem. Soc.*, 1841 (1949).
[19] H.M. Irving. *Q. Rev.*, **5**, 200 (1951).
[20] H. Irving, R.J.P. Williams. 'Liquid–liquid Extraction' In *Treatise on Analytical Chemistry*, Pt. 1, I. Kolthoff, P. Elving (Eds), Vol. 3, Interscience, New York (1961).
[21] D. Dyrssen. *Svensk. Kem. Tidskr.*, **68**, 212, [CA 50 14147 (1956)] (1956).
[22] J. Stary. *Chem. Listy*, **53**, 556, [CA 54 48 (1960)] (1959).
[23] A. Ringbom, E. Still. *Finska Kemistsamfundets Medd.*, **69**, 17, [CA 55 8223 (1961)] (1960).
[24] G.H. Morrison, H. Freiser. *Solvent Extraction in Analytical Chemistry.* Wiley, New York (1957).
[25] H. Irving, F.J.C. Rossotti, R.J.P. Williams. *J. Chem. Soc.*, 1906 (1955).
[26] J. Stary. *The Solvent Extraction of Metal Chelates*, Pergamon, London (1964).
[27] I.H. Scheinberg, A.G. Morell. *Ceruloplasmin*.In *Inorganic Biochemistry*, Vol. 1, G.L. Eichhorn (Ed.), Elsevier, New York (1973).
[28] N.N. Greenwood, A. Earnshow. *Chemistry of Elements*, Pergamon, New York (1984).
[29] M.A.H. Franson. *Standard Methods for Examination of Water and Waste Water.* 3–68, American Publication Health Associations, New York (1995).
[30] H. Bag, A.R. Turker, R. Coskun, M. Sacak, M. Yigitoglu. *Spectrochim. Acta, Part B*, **55**, 1101 (2000).
[31] H. Bag, A.R. Turker, M. Lale. *Talanta*, **51**, 1035 (2000).
[32] A.F. Soylak, M. Elci, M. Dogan. *J. Trace Microprobe Tech.*, **20**, 15 (2002).
[33] Y.H. Sung, Z.S. Liu, S.D. Huang. *Spectrochim. Acta, Part B*, **52**, 755 (1997).
[34] J. Rydberg, C. Musikas, G.R. Choppin. *Principles and Practices of Solvent Extraction*, Marcel Dekker, New York (1992).
[35] G.W. Gokel, J.E. Trafton. *Cation Binding by Macrocycles,* Marcel Dekker, New York (1990), 253.
[36] K. Shimizu, A. Furuhashi. *Bull. Chem. Soc. Jpn.*, **57**, 3593 (1984).
[37] J. Sandihigraha, P.V.R. Bhaskara Sarma. *Hydrometallurgy*, **45**, 211 (1997).
[38] I.L. Dukov, S. Guy. *Hydrometallurgy*, **8**, 77 (1982).
[39] K. Inoue, H. Tsunomach. *Hydrometallurgy*, **13**, 73 (1984).
[40] C. Pazos, R.M. Diaz, J. Coca. *J. Chem. Technol. Biotechnol.*, **36**, 79 (1986).
[41] G.H. Jeffery, J. Bassett, J. Mendham, R.C. Denney. *Vogels Textbook of Quantitative Chemical Analysis*, 5th Edn Edn, Wiley, New York (1991).
[42] A. Shokrolahi, M. Ghaedi, H. Ghaedi. *J. Chin. Chem. Soc.*, **54**, 933 (2007).
[43] J.M. Ouyang. *Solvent Extr. Exch.*, **17**, 1255 (1999).
[44] J. Aggett, R.A. Richardson. *Anal. Chim. Acta*, **50**, 269 (1970).
[45] J. Aggett, R.A. Richardson. *Anal. Chim. Acta*, **51**, 528 (1970).
[46] I. Stronsky, M. Rekas. *Radiochem. Radioanal. Lett.*, **14**, 297 (1973).
[47] J. Aggett, R.A. Richardson. *Analyst (London)*, **105**, 1118 (1980).
[48] J. Aggett, A.W. Khoo, R.A. Richardson. *J. Inorg. Nucl. Chem.*, **43**, 1867 (1981).
[49] C.R. Panda, V. Chakravortty, K.C. Dash. *J. Radioanal. Nucl. Chem.*, **108**, 65 (1987).
[50] N. Hirayama, I. Takeuchi, T. Honjo, K. Kubono, H. Kokusen. *Anal. Chem.*, **69**, 4814 (1997).
[51] K. Kubono, N. Hirayama, H. Kokusen, K. Yokoi. *Anal. Sci.*, **17**, 193 (2001).
[52] N. Hirayama, J. Taga, S. Oshima, T. Honjo. *Anal. Chim. Acta*, **466**, 295 (2002).
[53] W.A. Zoubi, F. Kandil, M.K. Chebni. *Arabian J. Chem.*, xxx, xxxx (in press).
[54] S. Oshima, N. Hirayama, K. Kubono, H. Kokusen, T. Honjo. *Talanta*, **59**, 867 (2003).
[55] S.Z. Zahra, Y. Mohammad Reza. *Iran. J. Chem. Chem. Eng.*, **29**, 11 (2010).
[56] N.J. Parmar, H.A. Barad, B.R. Pansuriya, R.A. Patel. *J. Coord. Chem.*, **64**, 688 (2011).
[57] Y. Boukraa, T. Benabdallah. *J. Coord. Chem.*, **64**, 832 (2011).
[58] C.R. Panda, V. Chakravortty, K.C. Dash. *Indian J. Chem., Sect A*, **24**, 807 (1985).
[59] S.A.M. Fathi, M. Parinejad, M.R. Yaftian. *Sep. Purif. Technol.*, **64**, 1 (2008).
[60] K. Saberyan, E. Zolfonoum, M. Shamsipur, M. Salavati-Niasari. *Sep. Sci. Technol.*, **44**, 1851 (2009).
[61] D. Kara, M. Alkan. *Microchem. J.*, **71**, 29 (2002).
[62] B. Ziyadanogullari, D. Cevizici, H. Temel, R. Ziyadanogullari. *J. Hazard. Mater.*, **150**, 285 (2008).
[63] K. Saberyan, M. Shamsipur, E. Zolfonoun, M. Salavti-Niasari. *Bull. Korean Chem. Soc.*, **29**, 94 (2008).
[64] B. Dede, F. Karipcin, M. Cengiz. *J. Chem. Sci.*, **121**, 163 (2009).
[65] H. Kanttekin, U. Ocak, Y. Gok, I. Acar. *J. Inc. Phenom.*, **48**, 95 (2004).
[66] I. Yilmaz, H. Temel, H. Alp. *Polyhedron*, **27**, 125 (2008).
[67] A. Asharf. *Tetrahedron*, **60**, 1541 (2004).
[68] W.A. Zoubi, F. Kandil, M. Khaled Chebani. *Spectrochim. Acta, Part A*, **79**, 1909 (2011).
[69] B. Morkhtari, K. Pourabdollah. *J. Coord. Chem.*, **64**, 4029 (2011).
[70] J.C. Braley, J.C. Carter, S.I. Sinkov, K.L. Nash, G.J. Lumetta. *J. Coord. Chem.*, **65**, 2862 (2012).
[71] G.J. Lumetta, T.G. Levitskaia, S.L. Latesky, R.V. Henderson, E.A. Edwards, J.C. Braley, S.I. Sinkov. *J. Coord. Chem.*, **65**, 741 (2012).

Downloaded by [Renmin University of China] at 10:48 13 October 2013

[72] S.O. Ojwach, G.S. Nyamato, B. Omondi, J. Darkwa, A.O. Okoth. *J. Coord. Chem.*, **65**, 298 (2012).
[73] S.Y. Sahu, V. Chakravortty. *J. Radioanal. Nucl. Chem.*, **227**, 163 (1998).
[74] S. Oshima, N. Hirayama, K. Kubono, H. Kokusen, H. Honjo. *Anal. Chim. Acta*, **441**, 157 (2001).
[75] M.R. Yaftian, S. Rayati, R. Sfarbali, N. Torabi, H.R. Khavasi. *Transition Met. Chem.*, **32**, 374 (2007).
[76] D. Emaldi, M.R. Yaftian, S. Rayati. *Turk. J. Chem.*, **31**, 423 (2007).
[77] H.H. Ishii, H. Einaga. *The Analyst*, **94**, 1038 (1964).
[78] T. Benabdallah, A.H. Al-Tiar, H. Reffas. *S. Afr. J. Chem.*, **57**, 33 (2004).
[79] S. Abe, K. Fuji, T. Sono. *Anal. Chim. Acta*, **293**, 325 (1994).
[80] S. Abe, J. Mochizuki, T. Sono. *Anal. Chim. Acta*, **319**, 387 (1996).
[81] S. Abe, T. Sono, K. Fuji, M. Endo. *Anal. Chim. Acta*, **274**, 141 (1993).
[82] D. Black, A.J. Blake, R.L. Finn, L.F. Lindoy, A. Nezhadali, G. Roughnaghi, P.A. Tasker, M. Schroder. *Chem. Commun.*, **340**, (2002).
[83] S.G. Galbraith, P.G. Plieger, P.A. Tasker. *Chem. Commun.*, **2662**, (2002).
[84] H.A. Miller, N. Laing, S. Parsons, A. Parkin, P.A. Tasker, D.J. White. *J. Chem. Soc., Dalton Trans.*, 3773 (2000).
[85] Y.A. Zolotov, V.L. Inov, N.V. Nizeva, A. Formanovskii. *Dokl. Chem.*, **277**, 256 (1984).
[86] T. Matsushita, N. Kubono, M. Fujiwara, T.T. Shono. *Chem. Lett.*, **657**, (1984).
[87] M.S. EL-Shahawi. *Anal. Sci.*, **7**, 443 (1991).
[88] Y. Zolotov, E.I. Morosanova, S.G. Dmitrienko, A. Formanovskii, G.V. Ivanov. *Microchim. Acta*, **84**, 399 (1989).
[89] E.I. Morosanova, Y. Zolotov, V.A. Bodyna, A. Formanovskii. *Microchim. Acta*, **84**, 389 (1984).
[90] M. Hadh Youcef, D. Barkat, T. Benabdallah. *J. Saudi. Chem. Soc.*, **10**, 15 (2006).
[91] Y. Boukraa, D. Barkat, T. Benabdallah, A. Tayeb, M. Kameche. *Phys. Chem. Liq.*, **44**, 693 (2006).
[92] M.N. Patel, C.B. Patel, R.P. Patel. *J. Inorg. Nucl. Chem.*, **36**, 3868 (1974).
[93] M. Hadj Youcef, T. Benabdallah, H. Hikti, H. Reffas. *Solvent Extr. Ion Exch.*, **26**, 534 (2008).
[94] J. Ryberg, C. Musikas, G.R. Choppin. *Principals and Practices of Solvent Extraction*, Marcel Dekker, New York (1992).
[95] M. Tuzen, E. Melek, M. Soylak. *J. Hazard. Mater.*, **136**, 597 (2006).
[96] H.H. Rump, H. Krist. *Laboratory Manual for the Examination of Waste Water and Soil*, VCH, New York (1988).
[97] Z. Marczanko. *Separation and Spectrophotometric Determination of Elements*, Ellis Harwood, New York (1986).
[98] H. Onishi. *Photometric Determination of Traces of Metals*, Wiley-Interscience, New York (1984).
[99] A.M. Haji Shabani, S. Dadfarnia, Z. Shahbaazi, A.A. Jafari. *Bull. Chem. Soc. Ethiop.*, **22**, 323 (2008).
[100] B. Yamina, B. Tayeb. *J. Coord. Chem.*, **64**, 832 (2011).
[101] K. Kasahra, M. Endo. *Anal. Sci.*, **17**, a339 (2001).
[102] S. Radi, A. Ramdani, Y. Lekchiri, M. Morcellet, G. Crini, J. Morcellet, L. Janus. *Eur. Polym.*, **36**, 1885 (2000).
[103] S. Radi, A. Ramdani, Y. Lekchiri, M. Morcellet, G. Crini, L. Janus, M. Bacquet. *New J. Chem.*, **27**, 1224 (2003).
[104] F. Malak, A. Ramdani, S. Radi. *J. Chem. Res.*, **9**, 640 (2004).
[105] F. Malek, A. Ramdani, I. Zidane, A. Yahyi, S. Radi. *Tetrahedron*, **61**, 2995 (2005).
[106] S. Radi, A. Ramdani, Y. Lekchiri, M. Morcellet, G. Crini, J. Morcellet, L. Janus. *J. Chem. Res.*, **11**, 712 (2003).
[107] S. Radi, A. Ramdani, Y. Lekchiri, M. Morcellet, G. Crini, L. Janus. *Tetrahedron*, **60**, 939 (2004).
[108] S. Radi, A. Yahyi, A. Ramdani, I. Zidane, B. Hacht. *Tetrahedron*, **62**, 9153 (2006).
[109] S. Kedy, N. Almhna, F. Kandil. *Jordan J. Chem.*, **7**, 73 (2012).
[110] F. Kandil, M. Khaled Chebani, W. Al Zoubi. *ISRN Org. Chem.*, **2012**, 8, Article ID 208284 (2012).
[111] W. Al Zoubi, F. Kandil, M. Khaled Chebani. *Org. Chem. Curr. Res.*, **1**, 1 (2012).
[112] C. Vergel, C. Mendiguchia, C. Moreno. *Sep. Sci. Technol.*, **47**, 2430 (2012).
[113] B. Dede, F. Karipcin, M. Cengiz. *J. Hazard. Mater.*, **163**, 1148 (2009).
[114] S. Abe, J. Mochizuki, T. Sone. *Anal. Chim. Acta*, **319**, 387 (1996).
[115] S. Abe, T. Sone, K. Fujii, M. Endo. *Anal. Chim. Acta*, **274**, 141 (1993).
[116] S. Abe, K. Fujii, T. Sono. *Anal. Chim. Acta*, **293**, 325 (1994).
[117] D. Barkat, M. Kameche. *Phys. Chem. Liq.*, **45**, 289 (2007).
[118] U. Ocak, H. Alp, P. Gokce, M. Ocak. *Sep. Sci. Technol.*, **41**, 391 (2006).
[119] S.K. Sahu, V. Chakravortty. *J. Radioanal. Nucl. Chem.*, **227**, 163 (1998).
[120] D. Black, A.J. Blake, R.L. Finn, L.F. Lindoy, A. Nezhadali, G. Rougnaghi, P.A. Tasker, M. Schroder. *Chem. Commun.*, **340**, (2002).

Downloaded by [Renmin University of China] at 10:48 13 October 2013