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The synthesis of $(N_2O_2S_2)$ -Schiff base ligands and investigation of their ion extraction capability from aqueous media

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ABSTRACT

Two new Schiff bases (I) and (II) containing nitrogen–sulfur–oxygen donor atoms were designed and synthesized in a multi-step reaction sequence. The Schiff base (I) was used in solvent extraction of metal chlorides such as Cu^{2+} and Cr^{3+} as well as metal picrates such as Hg^{2+} and UO_2^{2+} from aqueous phase to the organic phase. The influences of the parameter functions, such as pH, solvent, ionic strength of aqueous phase, aqueous to organic phase and concentration of the extractant were investigated to shed light on their chemical extracting properties upon the extractability of metal ions. The effect of chloroform, dichloromethane and nitrobenzene as organic solvents over the metal chlorides extraction was investigated at 25 ± 0.1 °C by using flame atomic absorption and the result is that the ability of extraction in solvents as follows: $C_6H_5NO_2 > CHCl_3 > CH_2Cl_2$ and the compositions of the extracted species have been determined. The metal picrate extraction was investigated at 25 ± 0.1 °C by using sectrometry. As well that the extraction of picrates metal such as UO_2^{2+} and Hg^{2+} with Schiff base(I) in absence and presence of 2-(2-aminoethyl) pyridine was investigated in chloroform. The extraction results revealed the presence of neutral donors 2-(2-aminoethyl) pyridine shifts the extraction of UO_2^{2+} and Hg^{2+} by the studied Schiff base (I).

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1. Introduction

The field of solvent extraction, commonly called liquid–liquid extraction, has grown extensively in the past half century to become an economically significant family of techniques in industry, analytical chemistry and research. Moreover, liquid–liquid extraction has important applications in the removal of toxic metal ions from the environment and pollution prevention.

In addition, the Key to an efficient separation process is the development of extractant with a strong preference for relevant chemical species. Examples of such extractants include macrocyclic ligands, called crown ethers that bind metal ions such as sodium, potassium, lithium, cesium, strontium and barium [1–4]. An appropriate macrocyclic ligand exhibits good extraction selectivity for desired metal ion species. Recently, a crown extractant was used in the solvent extraction process for separating radioactive ¹³⁷Cs from the high-level wastes. Technetium is another element removed from alkaline nuclear-waste solution by the use of crown ethers.

Crown ethers were also used as spectrophotometric analytical reagents. For example, the use of some crown ethers for the

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measurement of lithium in biological samples has been reported [5]. Metal ions have enormous importance in many biological processes. Especially, heavy metal ions are effective enzyme inhibitors exerting toxic effects on living systems [6]. Therefore, separation and determination of toxic metal ions such as mercury, lead and cadmium in environmental sources play an important role for healthy life. Although the using of crown ethers in determination and separation of alkali metals has been thoroughly investigated, their usage as extractant for the mentioned toxic metals has relatively received little attention [7,8].

Moreover, lariat crown ethers which bear side-chain containing donor atoms possess unique cation binding properties compared with the parent crown ether containing no extra donor sites [9,10]. Also, as efficient organic ligands lariat crown ethers meet the requirement of rapid, strong and three-dimensional cation binding and mimic the properties of natural ionophores [11].

Furthermore, during the last decades considerable attention has been devoted to the chemistry of biscrown ethers for their applications in various area especially in ion-selective electrodes [12–15]. Most of the consideration has focused on macrocyclic receptors that tend to bind with more than one transition metal ion [16–22]. Especially, in the early 1990s, due to the soft donor functionality of sulphur atom, several research groups such as Robson [23], Schrode [24] and Brooker and co-workers [25], in 2000, achieved

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similar researches aimed at introducing thiophenolate head units into Schiff base macrocycles. In all actions, the thiophenolate analogues are expected to reveal very different properties (e.g. redox and magnetic) due to the presence of the very polarisable thiophenolate donors and their interest in thiolatebridged metal active sites in biology.

Moreover, biscrown ethers show extra binding properties than the monocrown ethers, where by the cooperatives action of two adjacent crown units, bis(crown ethers) tend to form stronger complexes with particular metal ion than the corresponding monocrown ethers, where it forms complexes with two crown moieties per cation: 'sandwich complexes' that improve the stability of the complex especially when the cation is too large to fit the cavity of the crown ethers [26,27].

Kantekin others have reported the use of $N_2O_2S_2$ Schiff base containing aromatic moieties for the transfer of various metal ions from the aqueous phase into the organic phase in liquid–liquid extraction system [28–30]. In this work, we have been interested in the design and synthesis of $N_2O_2S_2$ -crown ether extractants for the selected metal ions, which have bigger cavity size. The aim of this investigation is design and synthesis of two novel ligands, and also solvent extraction properties for the metal cations such as Cu²⁺, Cr³⁺, Hg²⁺, and UO₂²⁺ have been investigated.

2. Experimental

2.1. Reagents and apparatus

All the used chemicals were purchased from Aldrich or Merck unless otherwise cited. The C, H and N were analyzed on a Carlo-Erba 1106 elemental analyzer. The IR spectra of the ligands were recorded with a Midac 1700 instrument in KBr pellets. ¹H and ¹³C NMR spectra of ligands in CDCl₃ and C₂D₅OD solution were recorded on a Bruker 400 MHz spectrometer and chemical shifts are indicated in ppm relative to tetramethylsilane. Mass spectra were recorded using a KRATOS MS50TC spectrometer. AA 929 Unicam Spectrometer was used for FAAS measurements with an air-acetylene flame. The UV-vis measurements were recorded on a PerkinElmer λ 20UV-vis Spectrometer. A pH meter (Metrohm 691 pH Meter) was also used. All extractions were performed by using a mechanical flask agitator in 50 cm³ stoppered glass flasks.

2.2. Synthesis of α, α' -bis(5-bromo-2-carboxyaldehyde phenoxy)-1,4-xylene

To a stirred solution of 5-bromosalicylaldehyde (40 g, 200 mmol) and K₂CO₃ (13.8 g, 100 mmol) in DMF (100 ml) was added dropwise α, α' -dibromo-p-xylene. (17.5 g, 100 mmol) in DMF (40 ml). The reaction was continued for 4 h at 150–155 °C and then for 4 h at room temperature. Then, 200 ml distilled water was added and the mixture kept in refrigerator. After 1 h, the precipitate was filtered and washed with 500 ml water. It was dried in air and recrystalized from EtOH and filtered under vacuum. Yield: 80%, m.p. 228–230.

2.3. Synthesis of 1,7-bis(5-bromo-2-formylphenyl)-1,4,7-trioxaheptane

To a stirred solution of 5-bromosalicylaldehyde (40 g, 200 mmol) and K_2CO_3 (13.8 g, 100 mmol) in DMF (100 ml), was added dropwise 1-chloro-2-(2-chloroethoxy)ethane (14.3 g, 100 mmol) in DMF (40 ml). The reaction was continued for 4 h at 150–155 °C and then for 4 h at room temperature. Then, 200 ml distilled water was added and the mixture kept in refrigerator. After 1 h, the precipitate was filtered and washed with 500 ml

water. It was dried in air and recrystalized from EtOH and filtered under vacuum. Yield: 85%.

2.4. Synthesis of ligand

[N,N'-bis(2-aminothiophenol)- α , α' -bis(5-bromocarboxylidene phenoxy)-1,4-xylene] [H₂L]

A solution of α, α' -bis(5-bromo-2-carboxyaldehyde phenoxy)-1,4-xylene (10.0 mmol, 4.98 g) in 50 ml absolute ethanol was added dropwise over 2 h to a stirred solution of 2-aminothiophenol (20.0 mmol, 2.50 g) dissolved in 50 ml hot absolute ethanol. A solid mass separated out on cooling, which was kept in a refrigerator for better crystallization. It was then filtered and recrystallized from a mixture of absolute ethanol–DMF, yield 50%, m.p. 234–236. Anal. Calc. C, 56.98; H, 3.64; N, 3.91; S, 8.93. Found: C, 57.95; H, 4.06; N, 4.1; S, 9.5%.

2.5. Synthesis of ligand

[N,N'-bis(2-aminothiophenol)-1,7-bis(5-bromocarboxylidene phenyl)-1,4,7-trioxaheptane [H₂L]

A solution of 1,7-bis(5-bromo-2-formylphenyl)-1,4,7trioxaheptane (10.0 mmol, 4.7 g) in 50 ml absolute ethanol was added dropwise over 2 h to a stirred solution of 5-amino-1,3,4thia-diazole-2-thiol (20.0 mmol, 2.66 g) dissolved in 50 ml hot absolute ethanol. A solid mass separated out on cooling, which was kept in a refrigerator for better crystallization. It was then filtered and recrystallized from a mixture of absolute ethanol–DMF, yield 60%, m.p. 238–240. Anal. Calc. C, 37.39; H, 3.39; N, 11.89; S, 18.2. Found: C, 35.2; H, 2.2; N, 11.9; S, 18.13%.

2.6. Extraction procedure

Aqueous solutions containing 1.5×10^{-3} mol l⁻¹ metal chloride or metal picrate (aqueous solution (10 ml) containing 1.25×10^{-5} M picric acid and 1×10^{-2} M metal nitrate were placed in stoppered flask and shaken for 2 h at 25.0 ± 0.1 °C) in appropriate buffer were equilibrated with equal volumes of the chloroform. dichloromethane and nitrobenzene solutions of the Schiff base (I) 4×10^{-4} mol l⁻¹ by shaking in a mechanical shaker at 25 °C. Optimum equilibration time was determined for this system. In most cases distribution equilibrium was attained in less than 30 min and a shaking time of 120 min. The ionic strength of the aqueous was 0.1 M KCl in all experiments except those in which the effect of ionic strength was studied. After agitation, the solutions were allowed to stand for 120 min. The copper and chrome concentrations of the aqueous phase were determined by FAAS, and that of the organic phase from the difference by considering the mass balance. But the concentration of picrate ion remaining in the aqueous phase was then determined spectrophotometrically at 355 nm. Blank experiments showed that no picrate extraction The PH of aqueous phase was recorded as equilibrium PH.

The extractability of picrate (E%) was determined based on the absorbance of picrate ion in the aqueous from Eq. (1)

$$E\% = \left[\frac{(A_0 - A)}{A_0}\right] \times 100\tag{1}$$

where A_0 is the absorbance in the absence of ligand and A denotes the absorbance in the aqueous phase after extraction.

3. Results and discussion

3.1. Synthesis of Schiff bases

The synthetic experiments of new two Schiff bases (I) and (II) are shown in Scheme 1. The structure of novel compounds were



Scheme 1. Synthesis of Schiff bases (I) and (II).

characterized by a combination of elemental, IR, MS, ¹H NMR, ¹³C NMR spectral analyses data. The preparation of the Schiff bases illustrated in Scheme 1.

3.1.1. IR spectra

The spectrum showed a strong band at 1672 cm^{-1} in the spectrum of the Schiff base (I) are assigned to υ (C=N) of azomethine. A broad medium intense band was at 2930 cm⁻¹ due to methylene groups. The IR spectrum of the thio Schiff-base (I) exhibited a strong sharp band at 3400 cm⁻¹. This band was assigned to the stretching frequency of the N⁺H group, due to the presence of the intramolecular hydrogen bond (N-SH) in the molecule [29–31] (Scheme 1).

In the IR spectrum of Schiff base (II) the absence of band in the region \sim 3400 cm⁻¹ corresponding to free primary amine and hydroxyl group suggests that complete condensation of amino group with aldehyde. Appearance of a new strong absorption band

at 1607 cm⁻¹ attributable to characteristic stretching frequencies of the imino linkage ν (C=N) [32,33] provides strong evidence for the presence of product. The absorption in IR spectrum of Schiff base (II) at 2728 cm⁻¹ is due to the presence of SH. A broad medium intense band was at 3075 cm⁻¹ due to for aromatic protons.

3.1.2. Mass spectrum

The electron impact mass spectrum of the Schiff bases (I) and (II) confirm the probable formula by showing a peak at 716 amu, corresponding to the Schiff base (I) and 700 amu, corresponding to the Schiff base (II).

3.1.3. ¹H NMR spectra

The Schiff base (I) [Fig. 1(b)] exhibits signal at 5.38 ppm due to SH protons. It also exhibits resonance due to $-CH_2$ - protons around 1.57 ppm. The other characteristic resonance due to azomethine proton in Schiff base (I) appears at 8.73 ppm. Signals in the region 7–8.12 ppm due to aromatic protons [29–31].

The Schiff base (II) [Fig. 2(b)] exhibits signal at 5.3 ppm due to SH protons. It also exhibits resonance due to $-CH_2$ - protons around 3.8 and 1.1 ppm. The other characteristic resonance due to azomethine proton in Schiff base (II) appears at 8.86 ppm. Signals in the region 6.9–7.9 ppm due to aromatic protons [29–31].

3.1.4. ¹³C NMR spectrum

The ¹³C NMR (75 MHz, CHCl₃-d₁ 75 MHz) d (ppm) spectrum [Fig. 1(a)] of Schiff base (I) indicated new resonances are Arom: 114.19, 114.73, 121.31, 123.00, 124.53, 125, 126.18, 128.25, 132.20, 134, 135.93, 136.15, 151.96, 155.09. CH=N: 161.32. CH₂: 70.99.

The ¹³C NMR (75 MHz, C₂H₅OH-d₆ 75 MHz) d (ppm) spectrum [Fig. 2(a)] of Schiff base (II) indicated new resonances are CH₂: 79.92, Arom:110.57, 111.16, 11687.31, 118.90, 120.97, 127.72, 129.28, 131.56, 133.44, 137.55, 154.13, 159.82, 162.58, CH=N: 166.21.

3.2. Extraction of metal ions with Schiff bases

3.2.1. Effect of PH and solvents on the extraction of Cu(II) and Cr(III)

The stability of a transition metal complex with a polydentate chelate ligand depends on a range of factors including: number and type of the donor atoms present, the number and size of the chelate rings formed on complexation. In addition, the stability and selectivity of complexations strongly depend on the donor ability and dielectric constant of the solvent [34] and shape and size of the solvent molecules [35].

Generally, it is expected that in solvents with a high donor ability and dielectric constant, the stability constant of the complex should decrease due to the competition between the ligand and the solvent molecules for the metal ion. The donor ability of the solvent plays the most important role in the behavior of complexes reaction in nonaqueous solvents.

Fig. 3(C and D) shows the effect of PH on the extraction of Cu^{2+} and Cr^{3+} into chloroform, dichloromethane and nitrobenzene with Schiff base (I). As shown in figure the copper and chrome extraction is quantitative within the PH range of 6.1–7, 7.3–8.3 respectively. Besides, figure shows that the ability of extraction is better in the case of nitrobenzene solvent and this accords with what has been reported above.

3.2.2. Extraction of UO_2^{2+} and Hg^{2+} ions by H_2L in the presence of neutral donor ligand

The synergistic extraction (Fig. 4) of metal chelates has been mostly explained by an increase in hydrophobicity of extracted chelates by a replacement reaction of water molecules bound



Fig. 2. (a) ¹³C NMR (B) and (d) ¹H NMR (A) spectra of Schiff base (II).

to the central metal ion by basic neutral organic molecules (2-(2-aminoethyl)pyridine). Keep in mind the presence of water molecules in the structure of extracted species (Eq. (2)), one can consider an enhancement of extraction efficiency in the presence of a synergistic agent. To examine this suggestion, the effect of neutral donor on the extraction of uranium and mercury ions by Schiff base (I) was investigated (Fig. 4). The neutral donor was 2-(2-aminoethyl)pyridine. Considering the participation of a neutral



Fig. 3. Effect of pH and Solvents on the extraction of Cu²⁺ (C), Cr³⁺ (D), [📥] nterbenzene, [📕] chloroform, [📕] dichloromethane, Schiff base (I).



Fig. 4. Effect of pH on the extraction of UO_2^{2+} , S = (2-(2-aminooethyl)pyridine), organic solvent: chloroform, Schiff base (I).

donor molecule (S) in the extracted species of synergistic extraction process, the corresponding equilibrium reaction can be shown as: Considering the participation of a neutral donor molecule (S) in extracted species of synergistic extraction process, the corresponding equilibrium reaction can be shown as:

$$M_{aq}^{2+} + H_2L + S_{org} + PIC^{2-} \Leftrightarrow MLPICS^{\bullet}2H_2O_{org} + 2H_{aq}^{+}$$
(2)

its equilibrium constant is defined as Eq. (6):

$$K_{\rm syn} = \frac{[MLPicS^{\bullet}2H_2O]_{\rm org}[H^+]_{\rm aq}}{[M^{2+}]_{\rm aq}[H_2L]org[S]_{\rm org}[Pic^-]_{\rm aq}}$$
(3)

3.2.3. Effect of ionic strength of aqueous phase

The influence of KCl in the concentration range of 0.1–1.0 M on the extraction efficiency of Cu^{2+} and Cr^{3+} were studied in solutions containing 1.5×10^{-3} M Cu^{2+} and Cr^{3+} with 4×10^{-4} M Schiff base (H₂L) in organic phase. The extraction efficiency decreases with increase in ionic strength of the aqueous medium. Taking into account Eq. (4), the extraction constant (K_{ext}^0) at zero ionic strength for this reaction can be correlated with the ionic strength (I) by

$$\operatorname{Cu}_{(w)}^{2+} + \operatorname{H}_2 \operatorname{L}_{(o)} \rightleftharpoons \operatorname{Cu}_{(o)} + 2\operatorname{H}^+$$
(4)

$$K_{ext}^{0} = K_{ext} \frac{\gamma_{\rm H^{+}}^{2}}{\gamma_{\rm Cu^{2+}}}$$
(5)

$$K_{ext} = K_{ext}^{0} \frac{\gamma_{Cu^{2+}}}{\gamma_{H^{+}}^{2}}$$
(6)

According to the Debye-Huckel limiting law given

$$\log \gamma_{\pm} = -0.5 Z_i^2 \sqrt{I} \tag{7}$$



Fig. 5. Effect of A/O on the extraction of Cu^{2+} , organic solvent; chloroform, Schiff base.



Fig. 6. Effect of time on the extraction of $\mbox{Cu}^{2+},$ organic solvent: chloroform, Schiff base.

The activity coefficient (γ_{\pm}) decreases with increase in ionic strength. At the constant PH, the activity coefficient of Cu²⁺ and Cr³⁺ decreases as the ionic strength increase, hence K_{ext} decreases.

3.2.4. Effect of aqueous to organic phase

Phase ratio (A/O) is one of the factors that affect the extraction efficiency. The extraction efficiency, E% can be represented by [36].

$$E\% = \frac{D}{D + A/O} \times 100 \tag{8}$$

where *D* is the distribution ratio, *A* and *O* are the volumes of the aqueous and organic phases, respectively. Equation indicates that



Fig. 7. The plot of log D vs. pH at Constant Schiff base (I) (🗖) chloroform (🗖) dichloromethane (🗐) nterbenzene.



Fig. 8. Log D versus Log[Ligand(I)] for the extraction of Cu^{2+} and for Cr^{3+} ,organic solvent: dichloromethane.

the extraction efficiency decrease with increasing A/O ratio. Fig. 5 shown the effect of A/O on percentage extraction which was satisfied by Eq. (8).

3.2.5. A kinetic criterion of reagent stability

Fig. 6 shows that percentage of extraction decreases with shaking time and it also confirms that this Schiff base is decomposing during extraction.

3.2.6. Composition of the extracted species

The extraction constant of the species CuL is given by

$$K_{ext} = \frac{[CuL]_o[H^+]_w^n}{[Cu^{2+}]_w[H_nL]_o}$$
(9)

When CuL is the only extractable species and the metal is present in the aqueous phase predominantly as the cation Cu^{2+} , the metal distribution ratio (*D*) and the extraction constant are related by

$$\log D = \log K_{ext} + npH + \log [H_2L]_o$$
(10)

The effect of pH on the extraction of Cu²⁺ and Cr³⁺ ions from KCl media of ionic strength (*I*=0.1 M) has been studied, the logarithm of the *D* values obtained were plotted against the corresponding pH values (according to Eq. (10) a plot of log *D* against pH at constant 4×10^{-4} M of [H_nL]). A straight lines with a slopes of about (0.94, 0.7, 1.83) and (0.716, 0.757, 0.85) were obtained at *I*=0.1 of Cu²⁺ and Cr³⁺ respectively, as shown Fig. 7. The values represent the number of hydrogen ions released during the formation of metal–ligand complex and intercept log[H_nL] + log K_{ext}.

Fig. 8 shows the evolution of $\log D$ when increasing the concentration of H_2L at constant chloride concentration with dichloromethane as organic solvent. As seen from the plots, there is a linear relationship between $\log D$ and $\log[L]_{org}$, and the slope should be equal to the number of ligand molecules per cation in the extracted species. The slopes of lines are equal to 1.1 for dichloromethane. Therefore, ligand forms a 1:1 (L:M) complex with Cu^{2+} and Cr^{3+} .

4. Conclusion

In the first stage, substituted Schiff Base analogues are obtained from condensation of bis-aldehyde and aminothio in dry ethno. Then, Schiff bases are synthesized from a 2:1 mixture of 1 and 2 expected pcs. The high transfer of Cu^{2+} and Cr^{3+} ions from the aqueous phase to the chloroform, dichloromethane and nitrobenzene were observed with compound (H₂L) and results showed that the best order of solvents is as follows: $C_6H_5NO_2 > CHCl_3 > CH_2Cl_2$. The results indicate that H₂L in organic phase extracts efficiently Cu^{2+} and Cr^{3+} in aqueous phase containing 0.1 mol KCl in the pH range of approximately 6–7 and 7–8.5 respectively at 25 °C. And the results also show that this ligand is decomposing during extraction. The compositions of extracted Cu-complexes and Cr-complexes were 1:1 (L:M) for the ligand in dichloromethane.

The synergic extraction with the mixtures is due to formation of adduct ML(S). The synergic coefficient has high value in presence of 2-(2-aminoethyl) pyridine, since has the high basicity.

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