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Synthesis and characterization of triethylammonium 2-(diphenylphosphinoamino)-5-methylbenzenesulfonate and use of it as a new complexing agent in solvent extraction of Ni (II) ions from water

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ABSTRACT

Triethylammonium 2-(diphenylphosphinoamino)-5-methylbenzenesulfonate (2) has been synthesized by treating Ph_2PCl with 4-aminotoluene-3-sulfonic acid. The new compound was characterized by IR, ^1H- and ^{31}P-NMR, and elemental analysis. Liquid–liquid extraction of Ni (II) ions using synthesized aminophosphine derivative as new extractants was studied. The influence of critical parameters on the extraction properties of aminophosphine derivative such as solution pH and ligand mass were investigated. The liquid–liquid extraction ability of newly synthesized compound has also been compared another aminophosphine derivative (1). UV-vis spectrophotometry used to determine the liquid/liquid extraction efficiencies of Ni (II) metal ions at various conditions. Both of the extractant was found to be efficient for extraction of Ni (II) metal ions with recoveries of 84.8 and 81.5% for ligands 1 and 2 respectively.

Keywords: Aminophosphines; Organophosphorus compounds; Liquid–liquid extraction; Separation; Selectivity; Nickel

1. Introduction

Tertiary phosphine is a large class of fascinating ligands commonly used in coordination chemistry. They play an important role in areas ranging from homogeneous catalysis to selective metal extraction chemistry and to therapeutic applications [1]. If the phosphorus (III) centre is chemically bonded to an amino substituent (primary or secondary), results in "aminophosphine". Aminophosphines have proven their merits in various aspects of chemistry like sterochemistry, theoretical and computational chemistry, organometallic and coordination chemistry, and catalysis and inorganic heterocyclic chemistry [2].

Interest in phosphines with P–N bonds arises from the different electronic properties transferred by the nitrogen centre to the phosphorus centre(s) [3]. Small variations in the electron density on the donor atoms of these ligands can cause significant changes to their coordination behaviours and structural features of resulting complexes [4].

The extraction of metal cations from waters is a current topic by environmental consideration because of their harmful and toxic effects. In natural conditions, heavy metals are not biodegradable and they tend to accumulate in living organisms resulting in

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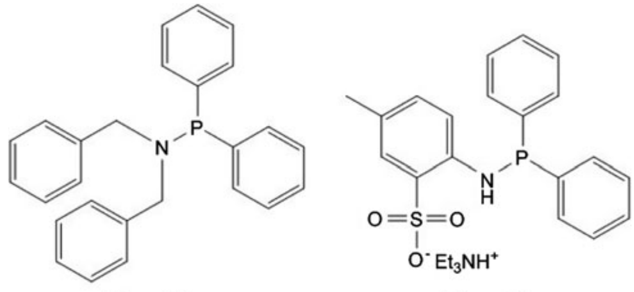
various diseases and disorders [5]. The presence of these metal ions in waters inhibits the natural biodegradation process of other pollutants, which possibily present in the waters. So their concentrations should be lowered to acceptable levels before discharging them to the environment [6]. There are several techniques that have been performed to develop efficient methods for metal extraction [7]. Most common of these techniques is solid-phase extraction [8–12], liquid–liquid extraction [13–16], cloud-point extraction [17–19] and electroanalytical-based techniques [20–21] that have been used for the removal of metal ions from waters.

Transportation of materials from one phase to another is the most fundamental procedure for the separation of chemical species from the matrix or from other co-existing components. The liquid–liquid extraction is widely used sample preparation technique, whose goal is cleanup, enrichment and signal enhancement [22]. This extraction technique is basically a three-step separation method. In the extraction step, the metal containing aqueous solution is contacted with an organic solution in which an extractant agent dissolved. The metal of interest reacts with the extractant and then is transferred from the aqueous to the organic phase. The liquid phases are separated and the organic phase loaded with target metal goes to the next step for determination process [23].

Herein, we describe the synthesis of new aminophosphine ligand and characterized by IR, ^{1}H NMR, ^{31}P NMR spectroscopic techniques and by elemental analysis. This paper also deals with the liquid–liquid extraction process of new ligand and its selectivity comparison with another aminophosphine derivative (N,N-dibenzyl-1,1-diphenylphosphinoamine, Fig. 1) which was synthesized our previous study [24].



Ligand 1 **Ligand 2**

Fig. 1. Chemical structures of N,N-dibenzyl-1,1-diphenylphosphinamine (1) and newly synthesized triethylammonium 2-(diphenylphosphinoamino)-5-methylbenzene sulfonate (2).

2. Materials and methods

2.1. Reagents and apparatus

Reactions were routinely carried out using Schlenk-line techniques under pure dry nitrogen gas. Solvents were dried and distilled prior to use. All other chemicals were used in analytical grade, without further purification. Melting points were determined by using Electrothermal A 9100 and are uncorrected. ^{31}P-{^{1}H} and ^{1}H NMR spectra were taken on Bruker UltraShield-400 spectrophotometer. Infrared spectra were recorded on a Perkin Elmer FT–IR System Spectrum BX. Elemental analysis was performed in a TruSpec Micro. Spectrophotometric measurements were performed by Shimadzu UV-160 A UV-vis spectrometer.

2.2. Preparation of triethylammonium 2-(diphenylphosphinoamino)-5-methyl benzene sulfonate

Triethylamine (3.8 mL, 27.41 mmol) and Ph_2PCl (2.5 mL, 13.60 mmol) were sequentially added with stirring to 4-aminotoluene-3-sulfonic acid (2.55 g, 13.62 mmol) solution in tetrahydrofuran (20 mL). The reaction mixture was stirred for 4 h and then filtered to remove $Et_3N.HCl$. The resulting solution was evaporated under reduced pressure and the product dissolved with diethyl ether in an acetone–dry ice bath. The mixture was allowed to warm slowly to room temperature. The solvent was removed under vacuum to give a white solid of the crude product, which was crystallized from CH_2Cl_2/diethyl ether mixture (2:1) at 0 °C. Yield 4.83 g (75%). m.p.: 188 °C. ^{1}H NMR (DMSO, δ, ppm): 10.17 (b, NH^+, 1H), 7.04–7.72 (m, Ph, 13H), 3.04 (q, $NH(\underline{CH_2}CH_3)_3^+$, 6H), 2.49 (s, NH, 1H), 2.31 (s, CH_3, 3H), 1.18 (t, $NH(CH_2\underline{CH_3})_3^+$, 9H), ^{31}P NMR ($CDCl_3$, δ, ppm): 23.5 (s). Selected IR (KBr pellet, cm^{-1}): 827 (PN). Elem. Anal.: $C_{25}H_{33}PN_2SO_3$ (472.58 $g mol^{-1}$) Found (Required): C, 63.21 (63.54); H, 6.78 (7.04); N, 5.51 (5.93); S, 6.25 (6.78).

2.3. Liquid–liquid extraction procedure

A 5×10^{-5} M aqueous solution of nickel picrate solution was prepared according to literature. 0.01 g of ligands 1 and 2 were separately dissolved in 100 mL dichloromethane and used as extractant. A 2 mL of metal solution and 2 mL of buffer solution (for pH adjustment) was added to 10 mL volumetric flask and filled with distilled water. A 2 mL of extractant solution was added to a 10 mL volumetric flask and completed with dichloromethane. Equal volumes (10 mL) of aqueous solution and the extracting solution were mixed in a 50 mL beaker and shaken with a magnetic stirrer at 25℃ for 2 h. Metal ion concentrations in the aqueous phase were determined by UV-vis spectrophotometry after phase separation. Metal ion extraction values (%E) in the aqueous phase were determined 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 triethylammonium 2-(diphenylphosphinoamino)-5-methyl benzene sulfonate

Although many synthetic methods like condensation, scrambling and transamination reactions are reported in the literature, the condensation route is the most widely used and the best one for synthesizing a wide variety of P(III)–N compounds [2]. The reaction of 4-aminotoluene-3-sulfonic acid with diphenylchlorophosphine affords the triethylammonium 2-(diphenylphosphinoamino)-5-methylbenzenesulfonate in good yield as shown in Fig. 2.

Among the routes used to prepare aminophosphines, the most frequently used method involves aminolysis of a chlorophosphine. The reaction of chlorophosphine and the primary amine usually provides the target compound, RNHPR′$_2$, in high yield. The reactions of some primary amine derivatives with Ph_2PCl in the presence of triethylamine have been thoroughly studied and different substances were obtained, depending on the relative ratio of the reagents, the electron-withdrawing groups and their positions on the aromatic ring and solvents such as diethyl ether and dichloromethane. Aminophosphines (Ph_2PNHR) are found as the main products, and when the reaction conditions changed, diphosphinoamines ($RN(PPh_2)_2$) or iminodiphosphines ($R–N=PPh_2-PPh_2$) are also formed as the major products [3]. The substituents at the amine backbone can also play an important role in determining the outcome of the products [25].

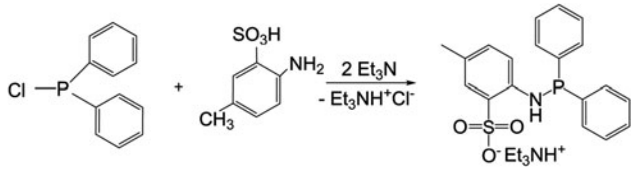


Fig. 2. Synthesis of triethylammonium 2-(diphenylphosphinoamino)-5-methyl benzene sulfonate.

We investigated the aminolysis reaction of 4-aminotoluene-3-sulfonic acid with Ph_2PCl in the presence of Et_3N in tetrahydrofuran as solvent. In general, aminodiphenylphosphines $RNHPPh_2$ give rise to singlet resonances between 25 and 35 ppm. Diphosphinoamines ($R–N(PPh_2)_2$) also exhibit a singlet resonance, but at higher frequency, typically around 64–70 ppm [5]. There was no evidence for the formation of iminodiphosphine, producing two sets of doublets at $\approx +10$ to ≈ -20 ppm [26]. The ^{31}P-{^1H} NMR spectrum of the aminophosphine shows singlet at 23.5 ppm. The ^{31}P-{^1H} NMR spectrum of the aminophosphine shows that the compound displays the characteristic signal of aminophosphine, and the result is in agreement with the earlier studies [3].

The ^1H NMR spectrum is consistent with the proposed structure. In the ^1H NMR spectrum of ligand, while the resonances due to aromatic protons appear in the range δ 7.0–7.7, NH signal was observed as singlet at 2.5 ppm. In addition, CH_3 signal is observed at 2.3 ppm. ^1H NMR spectrum shows that the ligand is in SO_3Et_3NH form. The signal at 10.2 ppm is assigned to the NH proton of Et_3NH^+. Methylenic ($–CH_2–$) protons of the triethylamine counterion of ligand are observed 3.0, where methyl ($CH_3–$) protons are at 1.2 ppm. In the IR spectrum of the ligand, the υ(P–N) vibration is tentatively assigned to a very strong absorption at 827 cm^{-1}.

3.2. The UV-vis analysis of Ni (II) picrate and extractants

Fig. 3 shows the individual UV-vis spectra of Ni (II) picrate, ligands 1 and 2. The significant maximum absorbance peaks appeared at 346, 238 and 237 nm respectively.

The UV-vis spectra of nickel picrate in dichloromethane after phase separation were proved that Ni

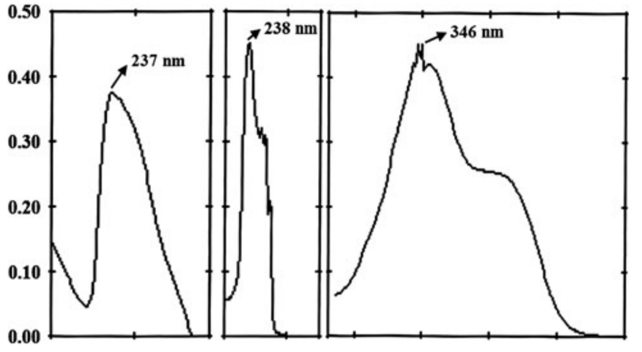


Fig. 3. The UV-vis spectra of ligands 1 and 2 and Ni (II) picrate in dichloromethane solution.

(II) ions formed complexes with both ligands 1 and 2 and these ligands carried the metal picrate into the organic phase. Because according to the blank test (without adding extractant), we observed that no peak was appeared at 346 nm.

3.2.1. *Effect of pH on the extraction of Ni (II)*

The effect of pH (water phase) on the extraction of Ni (II) with ligands 1 and 2 was studied to determine the optimum pH value required for extraction. Fig. 4 shows the dependence of recovery to solution pH.

It is obvious that pH is an important parameter in the extraction process of Ni (II) ions. Ligand 1 extracted 84.8% of Ni (II) at pH 7 and 84.6% at pH 4 as maximum. So, we have chosen the neutral pH as optimum for ligand 1. On the other hand, the extraction percentage of Ni (II) ions was drastically lowered with the raise of pH for ligand 2. Because of this, the optimum value was chosen as pH 4 where the recovery value was 81.5%.

3.2.2. *Effect of ligand volume on the extraction of Ni (II)*

The effect of ligand volume (organic phase) on the extraction of Ni (II) was studied to determine the optimum value required for extraction. Fig. 5 shows the dependence of recovery to ligand volume of organic phase.

According to Fig. 5, optimum ligand volume for both ligands 1 and 2 was 2 mL. The recovery values were 84.5 and 80.1 for ligands 1 and 2, respectively. Upon this value recoveries started to decrease.

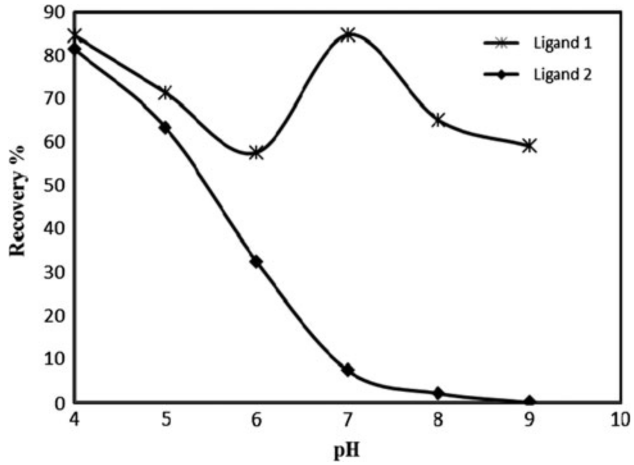


Fig. 4. Effect of solution pH on the recovery of Ni (II) ions.

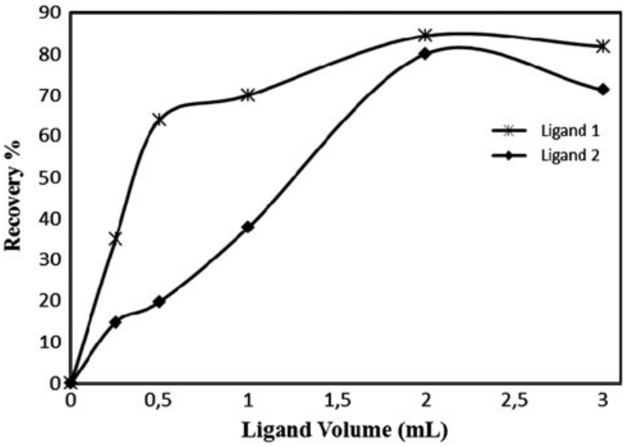


Fig. 5. Effect of ligand volume on the recovery of Ni (II) ions.

The mechanism of overall extraction process may be represented by the equation:

$$M^{n+}_{(aq)} + nPic^{-}_{(aq)} + mL_{(org)} \rightleftharpoons [M(Pic)_n(L)_m]_{(org)} \qquad (2)$$

Where L represents the extractant reagent and subscripts (aq) and (org) denotes the aqueous and organic phases, respectively.

4. Conclusions

A new aminophosphine derivative triethylammonium 2-(diphenylphosphinoamino)-5-methylbenzenesulfonate was successfully synthesized and characterized.

The newly prepared molecule was used as extractant for the recovery of Ni (II) ions in water. The extraction ability of the molecule was also compared another aminophosphine derivative.

Both of the extractant was found to be efficient for extraction of Ni (II) metal ions with recoveries of 84.8 and 81.5% for ligands 1 and 2, respectively.

Acknowledgements

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