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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

The Synthesis and Investigation of Liquid–Liquid Extraction Capability of *N*-Diphenylphosphino-*N*-ethylaniline and Its Chalcogenide Derivatives

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Abstract—The aminophosphine ligand was synthesized by the reaction of N-ethylaniline with chlorodiphenylphosphine in the presence of triethylamine at low temperature. Oxidation of the ligand with elemental sulfur or selenium afforded the corresponding aminophosphine sulfide and selenide. The compounds were characterized by elemental analyses, IR, ^{1}H and ^{31}P NMR. *N*-diphenylphosphino-*N*-ethylaniline and its chalcogen derivatives were used as ligands in solvent extraction of metal picrates such as Cd^{2+} and Ni^{2+} from the aqueous to the organic phase. Influences of parameters such as pH of the aqueous phase, solvent, extraction time, and extractant concentration were investigated to determine the extraction ability of ligands for metal ions. Results of the experiments showed that an extractability of 95.5 and 97.8%, respectively for Ni^{2+}, and Cd^{2+} at pH 2 could be achieved.

Keywords: Aminophosphines, chalcogenides, heavy metals, solvent extraction.

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Pollution caused by metal ions in wastewater is a common problem faced by many countries in recent years. Ni^{2+} and Cd^{2+} ions in wastewater have been especially recognized as key contaminants that damage the environment and adversely affect human health [1–6]. In spite of their toxicity, these metals are used in a wide variety of industries such as plating and cadmium–nickel battery, phosphate fertilizers, mining, pigments, stabilizers and alloys, and find their way to the aquatic environment through wastewater discharges [3, 7]. Therefore, the recovery of cadmium and nickel is necessary and very important to gain the metal values and protect the environment. From this point of view, in metal recovery, the solvent extraction is one of the favored separation techniques because of its simplicity, speed and wide scope [8–12]. Different types of extractants used for the extraction of Cd(II) and Ni(II) include amines, carboxylic acids, oximes and also organophosphorus extractants [8, 13]. Also synergistic extraction systems containing mixtures of organophosphorus extractants and amine extractants have been reported for the extraction and separation of the transition metal ions [14, 15].

Aminophosphines containing direct P–N bonds are a well-known class of phosphorus compound. Over the years, aminophosphine researches have gained prime importance because of their acting as versatile ligands in coordination chemistry; specific roles as catalysts for various organic reactions and easy conversion to chalcogenides, which possess ligating behavior, and hence they find applications in catalysis and electronic industries [16, 17]. Although aminophosphine ligands may be constructed in large quantities through the use of relatively simple condensation processes, and from inexpensive starting materials, there are limited studies focused on the possibility of effective use in the extraction process of metal ions of aminophosphines and chalcogenide derivatives [18].

In this study, a new aminophosphine ligand (*N*-diphenylphosphino-*N*-ethylaniline) and its sulfide and selenide derivatives was synthesized and used as ligands in solvent extraction of metal picrates (Ni^{2+} and Cd^{2+}) from the aqueous to the organic phase.

EXPERIMENTAL

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. ^{31}P and ^{1}H NMR spectra were taken on Bruker UltraShield-400 spectrophotometer. Infrared spectra were recorded on a Perkin Elmer FTIR System Spectrum BX. Spectrophotometric measurements were performed by Shimadzu UV-160 A UV-vis spectrophotometer.

Preparation of $Ph_2PN(C_2H_5)Ph$. Triethylamine (4.39 mL, 31.69 mmol) and Ph_2PCl (6.09 mL, 31.69 mmol) were sequentially added with stirring to a solution of *N*-ethylaniline (4 mL, 31.69 mmol) in THF (40 mL) at 0°C. The reaction mixture was stirred for 6 h and then it was filtered to remove precipitated triethylamine hydrochloride. The resulting solution was evaporated under reduced pressure and diethyl ether added (20 mL). The solvent was removed under vacuum to give a white solid of the crude product. The material was removed from the flask and washed with diethyl ether and dried in vacuo. 6 g (62%); m.p. 129–130 °C; ^{1}H NMR ($CDCl_3$) δ, ppm): 7.28–7.92 (m, 15H, aromatic), 3.39 (q, 2H, CH_2), 1.42 (t, 3H, CH_3); ^{31}P NMR ($CDCl_3$) δ/ ppm): 21.59 (s); IR (cm^{-1}): 1434 (PPh), 925 (PN); Found (Calc. for $C_{20}H_{20}PN$): C, 78.44 (78.67); H, 6.38 (6.60); N, 4.37 (4.59).

Preparation of $Ph_2P(S)N(C_2H_5)Ph$. *N*-diphenylphosphino-*N*-ethylaniline (1,3 g, 4.26 mmol) and S_8 (0.136 g, 4.26 mmol) were refluxed in toluene (30 mL) for 6 h. The reaction mixture was concentrated to ca. 1–2 mL in vacuo and diethylether (10 mL) was added. The precipitate was filtered and dried in air to yield 2 as a pale yellow solid. 1 g (70 %); m.p. 172–173°C; ^{1}H NMR ($CDCl_3$) δ, ppm): 7.28–7.92 (m, 15H, aromatic), 3.38 (q, 2H, CH_2), 1.41 (t, 3H, CH_3); ^{31}P NMR ($CDCl_3$) δ, ppm): 80.06 (s); IR (cm^{-1}): 1436 (PPh), 909 (PN), 655 (P=S); Found (Calc. for $C_{20}H_{20}NPS$): C, 71.47 (71.19); H, 5.68 (5.97); N, 3.84 (4.15).

Preparation of $Ph_2P(Se)N(C_2H_5)Ph$. *N*-diphenylphosphino-*N*-ethylaniline (1,0 g, 3.27 mmol) and grey Se (0.258 g, 3.27 mmol) were refluxed in toluene (30 mL) for 5 h. The reaction mixture was concentrated to ca. 1–2 mL in vacuo and diethylether (10 mL) was added. The precipitate was filtered and dried in air to yield 3 as a white solid. 0.9 g (56 %); m.p. 158–159°C; ^{1}H NMR ($CDCl_3$) δ, ppm): 7.28–7.91 (m, 15H, aromatic), 3.39 (q, 2H, CH_2), 1.43 (t, 3H, CH_3); ^{31}P NMR ($CDCl_3$) δ, ppm): 82.67 (s, J_{PSe} = 701 Hz); IR (cm^{-1}): 1437 (PPh), 899 (PN), 707 (P=Se); Found (Calc. for $C_{20}H_{20}NPSe$): C, 62.84 (62.50); H, 5.12 (5.25); N, 3.34 (3.64)

Solvent extraction procedure. Transition metal picrates were prepared by the stepwise addition of a 1×10^{-2} M of metal nitrate solution to a 2.5×10^{-5} M aqueous picric acid solution by shaking at 25°C for 1 h. The 1×10^{-2} M solutions of the ligands were separately prepared in dichloromethane and used as extractants. An organic solution (10 mL) of ligand and an aqueous solution (10 mL) containing 4 mL of the metal picrate solution and 6 mL of a buffer solution (for pH adjustment) were placed in a stoppered flask, and stirred with a magnetic stirrer at 25°C for 1 h in a water jacket. The mixture was allowed to settle for 30 min for the completion of phase separation. Then, after the two phases were separated completely, concentrations of the nickel(II) and cadmium(II) picrate remaining in the aqueous phase were determined spectrophotometrically at 359 nm and 360 nm which are wavelength of maximum absorption of metal picrates used in experiments, respectively. Blank experiments showed that no picrate extraction occurred in the absence of ligand. The percent of extraction *E* (%) has been calculated as:

$$E = \frac{A_0 - A}{A_0} \times 100, \qquad (1)$$

where A_0 is the absorbance in the absence of ligand and A denotes the absorbance in the aqueous phase after extraction. The picrate extraction studies were conducted on three different samples and the average value of percent picrate extracted, with a standard deviation, was calculated. UV–Vis spectroscopy is a very simple, accessible and convenient analytical instrument for quantitative detection of metals [19]. UV–Vis appears to be a convenient tool to study the distribution of metal picrates between non-aromatic organic solvents and aqueous solutions.

RESULTS AND DISCUSSION

In this work, *N*-diphenylphosphino-*N*-ethylaniline (**1**), was prepared via phosphination of *N*-ethylaniline, with one equivalent of Ph_2PCl in the presence of triethylamine

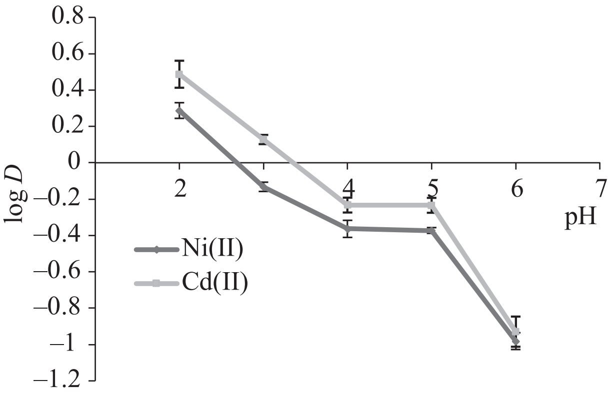


Fig. 1. Synthesis of the aminophosphine and its chalcogen derivatives.

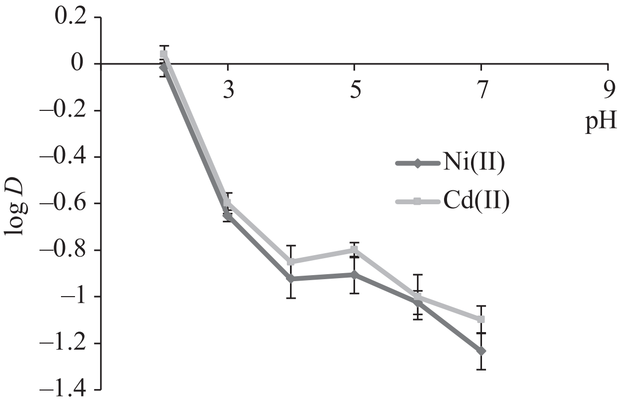


Fig. 2. Dependence of log D on pH for extraction of Ni^{2+} and Cd^{2+} picrates with $Ph_2PN(C_2H_5)Ph$ (**1**).

in tetrahydrofuran. Oxidation of 1 elemental sulfur or selenium gave the corresponding sulfide (**2**), and selenide (**3**), respectively (Fig. 1). The aminophosphine ligand and its chalcogen derivatives were characterized by elemental analyses, IR, ^1H and ^{31}P NMR.

The ^{31}P-{^1H} NMR chemical shift of **1** is found at 21.6 ppm whereas those of **2** and **3** occur at 80.06 and 82.67 ppm, respectively. The chemical shift values of **1–3** are in accordance with the literature [20]. The ^{31}P–{^1H} NMR spectrum of **3** consists of singlet with ^{77}Se satellites and the coupling constant value ($^1J_{PSe}$) is 701 Hz. The ^{1} H NMR spectra of **1–3** are consistent with the proposed structures. In the IR spectra of **1–3**, the υ(PN) vibration is observed at 925 cm^{-1} (for **1**), 909 cm^{-1} (for **2**), and 899 cm^{-1} (for **3**). The υ(P–Ph) bands are observed in region of 1435–1437 cm^{-1}. Also, the P=S and P=Se double bonds in **2** and **3** exhibit vibrations around 707 and 655 cm^{-1}, respectively.

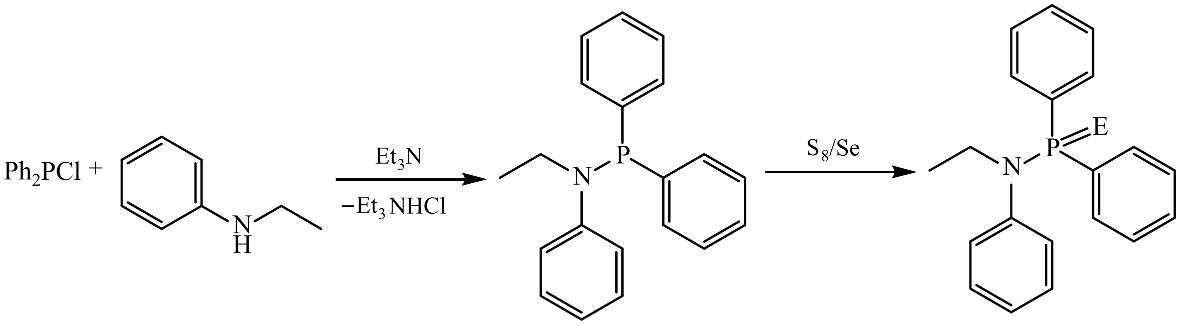
The liquid-liquid extraction of metal picrates such as Ni^{2+} and Cd^{2+} from aqueous phase to organic phase was carried out using aminophosphine (**1**) and its chalcogenide derivatives as ligands (**2** and **3**). The effects of several experimental parameters (pH, solvent, extraction time and extractant concentration) were investigated in order to find optimal operation conditions.

The effect of pH on the extraction of the metal picrates was investigated in the pH range from 1 to 7. The results indicate that the highest extraction efficiency was obtained at pH 2. Usually, as seen in Table 1 extraction to organic phase decreases as pH increases. When log *D*–pH graph is examined, this tendency is clear (Figs. 2–4). Here, *D* is the distribution ratio of metal picrates between the organic and the aqueous phase. Thus, in the further extraction studies, pH 2 was used.

For a good extraction efficiency the value of *D* should be greater than 1.0. Based on this criterion, it

Table 1. Effect of pH on the percentage extraction of Ni^{2+} and Cd^{2+} picrates with $Ph_2PN(C_2H_5)Ph$ (**1**), $Ph_2P(S)N(C_2H_5)Ph$ (**2**) and $Ph_2P(Se)N(C_2H_5)Ph$ (**3**) ([L] = 1 × 10^{-2} M in dichloromethane, the contact time: 1 h)

pH	Extractability, %					
	1		**2**		**3**	
	Ni^{2+}	Cd^{2+}	Ni^{2+}	Cd^{2+}	Ni^{2+}	Cd^{2+}
2	66.0 ± 3	75.4 ± 4	49.0 ± 3	52.3 ± 3	51.0 ± 2	62.2 ± 1
3	42.4 ± 2	57.3 ± 2	18.2 ± 1	20.1 ± 2	19.3 ± 2	40.7 ± 2
4	30.2 ± 3	36.9 ± 3	10.6 ± 2	12.3 ± 2	12.7 ± 1	33.5 ± 2
5	29.8 ± 1	36.8 ± 3	11.0 ± 2	13.7 ± 1	11.7 ± 2	35.2 ± 3
6	9.4 ± 1	10.5 ± 2	8.6 ± 1	9.1 ± 2	13.8 ± 1	36.2 ± 2
7	Not measured	Not measured	5.5 ± 1	7.4 ± 1	4.5 ± 1	14.4 ± 2



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E = S(**2**), Se(**3**).

Fig. 3. Dependence of log *D* on pH for extraction of Ni^{2+} and Cd^{2+} picrates with $Ph_2P(S)N(C_2H_5)Ph$ (**2**).

can be expected that a good extraction efficiency could be achieved in the extraction of Cd^{2+} and Ni^{2+} picrates at pH 2. The separation factor between the two metals was then calculated as the ratio of the distribution ratios of two metals ($SF_{Cd/Ni} = D_{Cd}/D_{Ni}$). Unlike the ligands **1** and **2**, selenide derivative (**3**) indicated a slight selectivity for Cd^{2+} over Ni^{2+} in the pH range of 4–7. The Cd/Ni separation factors are between 3.5 and 4.1 for ligand **3**.

Two different organic solvents, dichloromethane and chloroform, were used in the liquid–liquid extraction experiments. As shown in Table 2, chloroform gave the best extraction efficiency in case of using aminophosphine (**1**) as extractant. On the other hand, dichloromethane gave the best extraction efficiency for chalcogenide derivatives **2** and **3**. Thus, chloroform (for 1) and dichloromethane (for **2** and **3**) was selected as the solvent throughout the rest of the extraction study. The percentage of the extraction efficiency values of Cd^{2+} and Ni^{2+} ions with ligand **1** is higher than that of compounds **2** and **3** for both of the solvents. Also, the cation-binding affinities of all ligands for Cd^{2+} over Ni^{2+} in both organic solvents were found to be the highest.

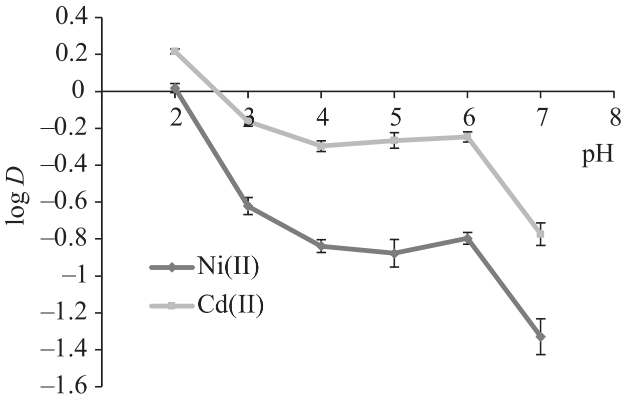

Fig. 4. Dependence of log *D* on pH for extraction of Ni^{2+} and Cd^{2+} picrates with $Ph_2P(Se)N(C_2H_5)Ph$ (**3**).

The effect of time on the extraction of metal picrates (Ni^{2+} and Cd^{2+}) with aminophosphine (**1**) and chalcogenide derivatives (**2**, **3**) was investigated. As shown in Table 3 and Figure 5, the best extraction time was 30 min when aminophosphine (**1**) was used as extractant for both metals, while it was 60 min for aminophosphine chalcogenides (**2** and **3**). The extraction efficiency decreased above these contact times. It is known that in some instances P–N bonds are sensitive towards acid- or base-catalyzed hydrolysis during complexation reactions [21]. Decreasing of extraction efficiency over time is possibly due to metal assisted hydrolysis of P–N bonds. In the following study, the extraction time was fixed to 30 and 60 min for ligand **1** and ligands **2**, **3** respectively.

When the ligand concentrations in organic phase was increased to 5×10^{-2} M, the extraction percentage values of Cd^{2+} and Ni^{2+} picrates were 97.8, and 95.5 for compound **1**, while 78.5, and 67.6 for compound **2**, and 86.2, and 73.8 for compound **3**, respectively.

The tested extractant ligands were found to be efficient for the liquid-liquid extraction of Ni^{2+} and Cd^{2+} picrates. All extraction efficiency values of *N*-diphenylphosphino-*N*-ethylaniline were higher than those of its chalcogenid derivatives (**2** and **3**). The greater degree to which this is observed in the aminophosphine (**1**) may be related to the stronger σ donor ability of aminophosphine (**1**) vs. its chalcogenid derivatives (**2** and **3**). On the other hand, the extraction efficiency values of Cd^{2+} picrate were higher

Table 2. Effect of solvent on the percentage extraction of Ni^{2+} and Cd^{2+} picrates with $Ph_2PN(C_2H_5)Ph$ (**1**), $Ph_2P(S)N(C_2H_5)Ph$ (**2**), and $Ph_2P(Se)N(C_2H_5)Ph$ (**3**) at pH 2 ([L] = 1 × 10^{-2} M; the contact time: 1 h)

Solvent	Extractability, %					
	1		**2**		**3**	
	Ni^{2+}	Cd^{2+}	Ni^{2+}	Cd^{2+}	Ni^{2+}	Cd^{2+}
Dichloromethane	66.0 ± 3	75.4 ± 4	49.0 ± 3	52.3 ± 3	51.0 ± 2	62.2 ± 1
Chloroform	69.1 ± 4	75.9 ± 4	20.4 ± 3	25.7 ± 2	26.2 ± 3	35.4 ± 1

Table 3. Effect of extraction time on the percentage extraction of Ni^{2+} and Cd^{2+} picrates with $Ph_2PN(C_2H_5)Ph$ (**1**), $Ph_2P(S)N(C_2H_5)Ph$ (**2**) and $Ph_2P(Se)N(C_2H_5)Ph$ (**3**) at pH 2 ([L] = 1 × 10^{-2} M; solvent: chloroform for ligand **1**, dichloromethane for ligands **2** and **3**)

Extraction time, min	Extractability, %					
	1		**2**		**3**	
	Ni^{2+}	Cd^{2+}	Ni^{2+}	Cd^{2+}	Ni^{2+}	Cd^{2+}
30	71.4 ± 2	76.8 ± 4	44.8 ± 2	48.1 ± 2	48.5 ± 3	53.7 ± 1
60	69.1 ± 4	75.9 ± 4	49.0 ± 3	52.3 ± 3	51.0 ± 2	62.4 ± 1
90	66.7 ± 4	67.4 ± 1	43.4 ± 3	47.0 ± 1	47.2 ± 1	51.5 ± 3
120	62.4 ± 3	67.1 ± 4	42.5 ± 4	45.9 ± 2	46.7 ± 2	50.8 ± 3

than that of Ni^{2+}, which can be explained by high affinity of “soft” phosphorus, or relatively less “softer” sulfur and selenium toward soft Cd^{2+} cations.

According to our results, ligands **1–3** were effective for extraction of metal ions at pH 2. In most of the industrial processes cadmium is present in acidic solutions and it becomes necessary to search for an extractant that can extract cadmium under these conditions [22]. Also, nickel is available in both leach liquors from ores and in secondary sources at lower pH. Most of the work in hydrometallurgy is related to extract metals at pH as low as possible [8]. *N*-diphenylphosphino-*N*-ethylaniline shows good efficiency and affinity for metal ions at pH 2 according to obtained results, which makes it suitable for solvent extractions in acidic media.

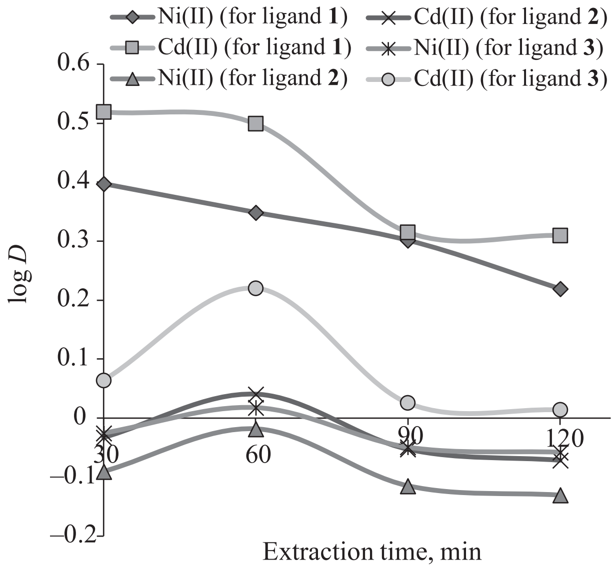

Fig. 5. Dependence of log *D* on extraction time for extraction of Cd^{2+} and Ni^{2+} picrates.

CONCLUSIONS

In conclusion, the synthesis and metal extraction abilities of *N*-diphenylphosphino-*N*-ethylaniline and its chalcogen derivatives were studied. The results showed that aminophosphine derivatives (**1–2**) are efficient ligands for the extraction of metal picrates such as Cd^{2+} and Ni^{2+} from an aqueous to an organic phase. The maximum extraction efficiency values of Cd^{2+} and Ni^{2+} picrates were 97.8, and 95.5 for *N*-diphenylphosphino-*N*-ethylaniline, while 78.5, and 67.6 for sulfide, and 86.2, and 73.8 for selenide, respectively, at pH 2. This makes the ligands suitable for solvent extraction study at low pH.

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CONFLICT OF INTEREST

The authors declare the absence of a conflict of interest that requires disclosure in this article.

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