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Extraction of metal ions (Co^{+2},Ni^{+2},Cu^{+2},Zn^{+2}) from their aqueous media using new Ligands derived from the organoPhosphorus Compounds and aniline

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ABSTRACT

The Ligand (I) was synthesized: *N*,*P*,*P*-triphenylphosphinothioic amide according to the reaction of diphenylphosphinothioic chloride with aniline, And the ligand (II) was synthesized: *O*,*O*-diphenyl phenylamidothiophosphate according to the reaction of *O*,*O*-diphenyl chlorothiophosphate with aniline.The correlations were identified by infrared spectroscopy FT-IR and proton magnetic resonance spectroscopy H-NMR, And identified some of the physical properties, such as: melting point, dissolution and color.

The Ligand were used to extract some of the transition metal ions from their aqueous media, studied the optimum time for extraction, which varied according to the associated and by meta. Study the variations of the logarithm of the distribution factor D in terms of the logarithm of the associated concentration and determine the ratio (Metal-Ligand)(1:2).

The percentage changes of the extraction were studied in terms of the changes in the pH, the effect of the place used was studied, and the comparison of the correlations with the extractive power was studied.

Keywords, aniline, Binary metal ions, Extraction, Factor D. OrganoPhosphorus

1- Introduction

Liquid-liquid extraction is a well-known technique in analytical chemistry.[1] This technique involves transferring the dissolved substance from the aqueous phase to the organic phase[2]Organophosphorus compounds containing electron-donor groups such as (O,S) were used in the extraction process,The organic chemistry of phosphorus depends on the presence of highly stable functional groups containing a bridge (phosphorus-sulfur or oxygen-carbon) or organic derivatives of phosphoric acid[3], Therefore, they are of great interest as they act as metal ion receptors, since the flexibility of these compounds enables them to extract metal ions from their aqueous environment, In the form of colored complexes that vary in color depending on the extracted ion and the degree of solubility in organic solvents. Organophosphorus compounds have contributed to coordination chemistry due to their stability at high oxidation states of ions. It possesses high thermal stability, which accounts for its diverse electronic and spatial properties. The complexes it forms with transition metal ions have been extensively studied[4]. The importance of extracts

stems from their potential use in multiple applied fields, such as element extraction in analytical chemistry, In their quantitative and qualitative determination, in their blocking, and in the active transport of cations across liquid membranes, they mimic some bioactive ionophores that perform active transport in biological systems and act as phase-transfer mediators in organic reactions. They are also used to determine the concentration of heavy metal ions harmful to the environment, And in isolating them from contaminated water [5]. Therefore, in this work, we synthesized new organophosphorus ligands and identified them using different spectroscopic methods. They were used to extract some of the transition metal ions from their aqueous solutions (chlorides), which will be the basis for synthesizing complexes in subsequent studies.

2-The importance and objective of the research

1- The importance of the research stems from the importance of binary transition metals in coordination chemistry.
2-Synthesizing new organophosphorus ligands by reacting them with aniline and using them in the extraction of some transition metal ions. Determining some of their physical and chemical properties according to the available techniques.
3-The possibility of obtaining (metal-organic) complexes comparable to complexes prepared by other methods.

3-Materials and research methods

3-1-Chemicals used:

1. Diphenylphosphine Chloride 95% 2. Benzene 98% 3. Absolute Ethanol 100% 4. Diphenylchlorophosphate 99.5% 5. Sodium Hydroxide 99.5% 6. Anhydrous Copper Chloride 99% 7. Sulfur 99% 8. Anhydrous Cobalt Chloride 99% 9. Anhydrous Nickel Chloride 99% 10. Toluene 99% 11. Dichloromethane 99.5% 12. Chlorfoam 100% () 13. Sulfuric Acid 96% 14. Calcium Chloride 95% 15. Acetic Acid 65% European 16 - Sodium Acetate, 99.5% purity; European 17 - Hydrochloric Acid , 36% purity; European 18 - Aniline

3-2- Equipment used in the research

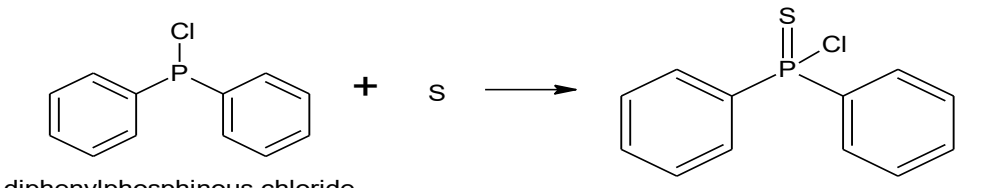
.1-Jascow-Infrared Spectrophotometer Fourier Transform FT/IR- spectrum – 460 plus
2-Electrothermal Melting Point Apparatus
3-Agimatic P-Selecta 24
4-Sartorius
5-MP225-PH meter PH
6-UV- visible spectrophotometer
7-(400 MHz4) ^{1}H-NMR
4-Research methods

4-1-Synthesis of organic ligands

4-1-1- Ligand(I): *N*,*P*,*P*-triphenylphosphinothioic amide

4-1-1-1-diphenylphosphinothioic chloride $(Ph)_2PSCL$

Take 50 ml of diphenylphosphine chloride using a pipette, That is equivalent to 0.26 g It was added to a two-necked flask containing a mixture of benzene and sulfur, The mixture was prepared by taking 8.5 g, equivalent to 0.26 mol, in 250 ml of pure benzene. Heat the mixture to boiling in the presence of a reversible condenser for three continuous hours, or heat until the sulfur is completely dissolved. Then remove the unreacted sulfur by filtration. Benzene is evaporated in a rotary evaporator, leaving a viscous, yellow liquid. The reaction yield was 93%. Its molecular weight is 252 g/mol.
The reaction is described by the following equation:



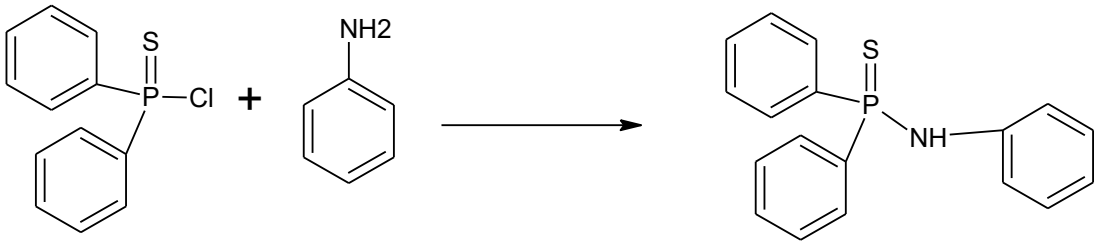
diphenylphosphinous chloride

diphenylphosphinothioic chloride

4-1-1-2-N,P,P-triphenylphosphinothioic amide

A quantity of diphenylphosphenethioic chloride $(Ph)_2PSCL$, amounting to 2.52g (equivalent to 0.01mol), is dissolved in pure benzene in a 500ml flask fitted with two necks, so that approximately 200ml of benzene is taken. We install a reflux condenser at the top of which a funnel containing calcium chloride is placed. A quantity of aniline, 0.92g (equivalent to 0.01mol), is prepared in a drip funnel. The flask containing diphenylphosphenethioic chloride is heated to 35°C with continuous stirring for approximately one hour. Then, the aniline in the drip funnel is added very slowly for one hour. After the addition is complete, the temperature is raised to 55°C while continuing to stir. Heating continues for three hours. After confirming the reaction is complete, heating is stopped and the mixture is cooled to room temperature. Excess benzene is evaporated under reduced pressure. A brown precipitate is formed and recrystallized with pure ethyl alcohol.

The reaction is described by the following equation:

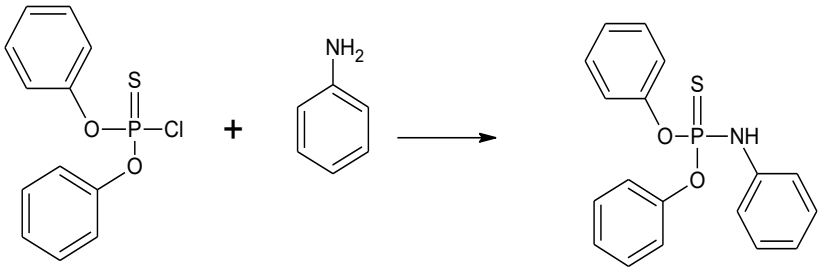


N,P,P-triphenylphosphinothioic amide

Physical properties of the Ligand: *N,P,P*-triphenylphosphinothioic amide:
It is soluble in dichloromethane, has a melting point of 92°C, and is brown in color. Its molecular weight is 309.3 g/mol, and its overall formula is C18H16NPS.

4-1-2- Ligand(II): *O,O*-diphenyl phenylamidothiophosphate

It is prepared using the same method as before, where 2.84 g (0.01 mol) of diphenylchlorophosphate (PhO)2PSCL is dissolved in pure benzene in a 500 ml flask with two necks. Approximately 200 ml of benzene is taken, and a reflux condenser is attached to its top. A funnel containing calcium chloride is placed on top of the condenser. 0.92 g (0.01 mol) of aniline is prepared in a drip funnel**.**
The flask containing diphenylchlorophosphate is heated to 35°C with continuous stirring for approximately one hour. Then, the aniline from the drip funnel is added very slowly over one hour. After the addition is complete, the temperature is raised to 55°C while continuing to stir. Heating is then maintained for three continuous hours. Once the reaction is confirmed to be complete, heating is stopped, and the mixture is cooled to room temperature. Excess benzene is evaporated under reduced pressure. A brown compound precipitates and is recrystallized with pure ethyl alcohol.
The reaction is described by the following equation:



Physical properties of the Ligand: *O*,*O*-diphenyl phenylamidothiophosphate
It is soluble in dichloromethane, has a melting point of 98°C, and is brown in color. Its molecular weight is 341.36 g/mol, and its molecular formula is C18H16NO2PS

4-2-Ion extraction process:

The extraction of ions from their aqueous medium is carried out using organic ligands present in a suitable organic solvent. The optimal equilibrium time of the two phases (organic and aqueous) for the extraction process is determined, and the extraction changes are studied by changing the pH of the medium while keeping the concentration of the ligand in the organic phase constant. The extraction changes are also studied by changing the concentration of the ligand while keeping the pH constant and the concentration of metal ions constant in the aqueous phase

4-3- Extraction equations, distribution coefficient, and extraction constant:

The following equation represents the reaction between the metal ion and the organic ligand, denoted by HL

$$M^{n+} + nHL \rightleftharpoons \overline{ML_n} + nH^+$$

Distribution factor (D):

$$D = \frac{[\overline{ML_n}]}{[M^{n+}]}$$

It represents the ratio of cation concentrations between the aqueous and organic phases and is calculated using the following relationship:

$$K_{Ex} = \frac{[\overline{ML_n}]\cdot[H^+]^n}{[M^{n+}]\cdot[\overline{HL}]^n} \Rightarrow D = K_{Ex}\cdot\left(\frac{[\overline{HA}]}{[H^+]}\right)^n$$

When we take the natural logarithm of the previous relationship, we obtain the following equation

$$\log D = \log K_{Ex} + n\log[\overline{HA}] - n\log[H^+]$$

When studying the changes in the logarithm of concentration associated with the changes in the logarithm of the distribution coefficient, we obtain a straight line of slope n which determines the ratio (associated: ion).

Extraction Percent (P%)

The percentage of the relationship was calculated:

$$P\% = 1 - \frac{1}{(1+D)} \times 100$$

5- Results and discussion:

5-1- Spectral study of artificial ligands:

5-1-1- IR Spectrum Study of Correlates:

The infrared spectra of the Ligand (I) and Ligand (II) were taken using an FT/IR device with a hard disk compression technique and the use of KBr, where the mixing ratio of the studied sample with the amount of KBr was (1:100) parts.

Figure (1) shows the absorption spectrum of the Ligand (I) using infrared radiation:

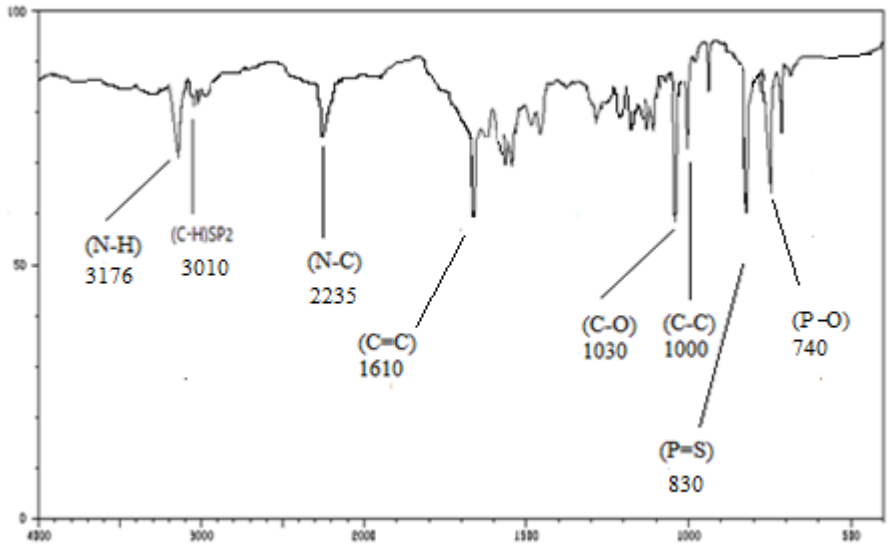


Figure (1) Absorption spectrum of the Ligand (I) in an FT-IR device

The spectrum shows an absorption band belonging to the N-H group at wavenumber 13176ν cm^{-1}, an absorption band belonging to the C-N bond stretching at wavenumber 2235ν cm^{-1}, an absorption band belonging to the C-O bond stretching at wavenumber 1030ν cm^{-1}, and an absorption band belonging to the SP2 hybridized C-H bond stretching at wavenumber 3010ν cm^{-1}. The spectrum also shows two absorption bands belonging to the P=S and P-O bond stretching at wavenumbers ν = 830ν cm^{-1} and ν = 740ν cm^{-1}, respectively. These are listed in Table 1.

Table (1) Interpretation Spectrum of Absorption Spectrum for the Ligand (I) using Infrared Radiation

Functional group	(C-N)	(C-O)	(P-O)	(P=S)	$(C-H)SP^2$	(N-H)
stretching	2235	1030	740	830	3100	3176

Figure (2) shows the absorption spectrum of the Ligand (II) using infrared radiation:

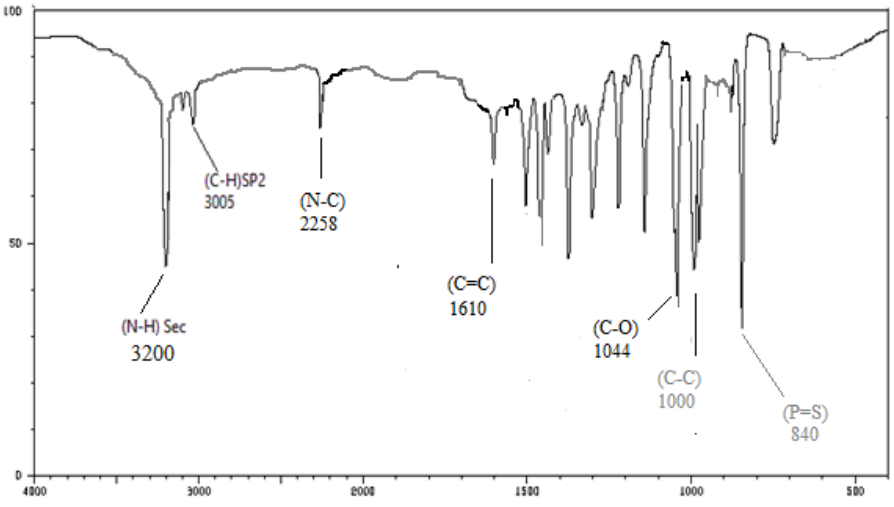


Figure (2) Absorption spectrum of the Ligand (II) in an FT-IR device

The spectrum shows a high-intensity absorption band due to the stretching of the (N-H) group at wavenumber $\bar{\upsilon}$ = 13200 cm^{-1}, and an absorption band due to the (C=C) group at wavenumber $\bar{\upsilon}$ = 11610 cm^{-1}. The spectrum also shows an absorption band due to the stretching of the aromatic (C-H) bond at wavenumber $\bar{\upsilon}$ = 3005 cm^{-}

[1], and an absorption band due to the (C-N) group at wavenumber $\bar{\upsilon}$ = 2258 cm^{-1}. Absorption bands due to (C-C) and (C-O) appear at wavenumbers $\bar{\upsilon}$ = 1000 cm^{-1} and $\bar{\upsilon}$ = 1044 cm^{-1}, respectively, and the (P=S) group appears at wavenumber $\bar{\upsilon}$ =-840 cm^{-1}. These are listed in Table (2).

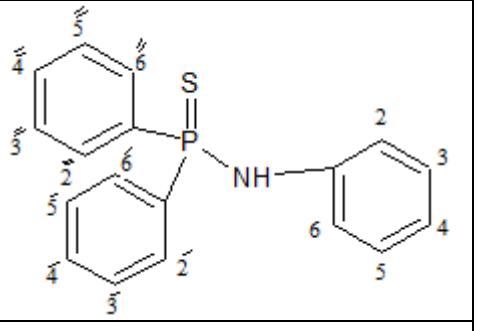
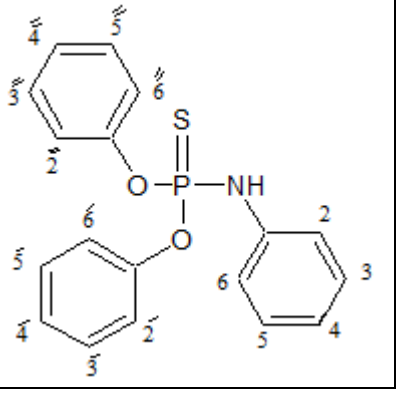
Table (2) Interpretation Spectrum of Absorption Spectrum for the Ligand (II) using Infrared Radiation

Functional group	(C-N)	(P=S)	(C-O)	(C-H)SP^2	(N-H)
stretching	2258	840	1044	3005	3200

5-1-2- Study of ^{1}H-NMR spectra of the ligands:

Nuclear magnetic resonance spectra of the ligands were recorded using a DMSO solvent

Table (3) Interpretation of the ^{1}H-NMR nuclear magnetic spectrum for ligand (I) and ligand (II):

^{1}H-NMR(DMSO) (δ ppm)	4(S,1H,NH) 6.63(d,2H,C2,C6) 6.81(d,1H,C4) 7.20(m,2H,C3,C5) 7.45(m,6H,C2′,C6′,C4′,C4″ C2‴, C6‴) 7.77(m,4H,C3′,C5′, C3‴, C5‴)	
	4(S,1H,NH) 6.63(d,2H,C2,C6) 6.81(d,1H,C4) 7.20(m,2H,C3,C5) 7.18(d,2H,C4′,C4″) 7.21(m,4H,C2′,C6′, C2‴, C6‴) 7.28(m,4H,C3′,C5′, C3‴, C5‴)	

5-2-practical study of extraction using artificial ligands

5-2-1- A study ligand to extraction processes

5-2-1-1- Results of a study on the effect of shaking time on the extraction of ions (II) using the ligand (I)

Solutions of 3 × 10^{-3} M of ligand (I) prepared in dichloromethane (CH_2Cl_2) and aqueous solutions of divalent metal ions of 3 × 10^{-3} M at pH = 7 at laboratory temperature (25°C) were used. The extraction process was carried out in 50 mL graduated tubes tightly sealed with glass stoppers at room temperature, with horizontal mixing. A series of tubes were used, and 5 mL of the aqueous solution was placed in each tube along with 5 mL of the organic solution, according to the concentrations indicated in the experimental work, and the extraction process was performed. After 5 minutes, a sample of the aqueous phase is taken from the first tube, and the absorbance is measured at a wavelength of λmax 540 using a spectrophotometer while extraction continues in the remaining tubes. Then, after 10 minutes, a sample of the organic phase is taken from the second tube, and the absorbance is measured while extraction continues in the remaining tubes. The extraction process is repeated for a period of time until a stable absorbance value is obtained. The ion concentration in the organic medium is calculated by subtracting the total ion

concentration in the aqueous medium before extraction from the ion concentration in the aqueous medium after extraction. The extraction process is repeated three times.

We obtained the results shown in the following tables:

Table (4) Effect of mixing time on the extraction process of metal ions (II) using the ligand (I).

n=3 a=0.95 $C_{ion}=1\times10^{-3}$ $C_{leg}=3\times10^{-3}$ pH=7

P%				
Co^{+2}	Ni^{+2}	Cu^{+2}	time	
5.9	6.8	9.1	5	1
10.28	12.78	22	10	2
15.32	24.7	27	15	3
29.47	35.89	39.48	20	4
37.46	41.89	52.6	25	5
45.34	50.34	59.82	30	6
52.94	59.8	64.7	35	7
58.57	63.75	69.4	40	8
60	64.78	70.1	45	9

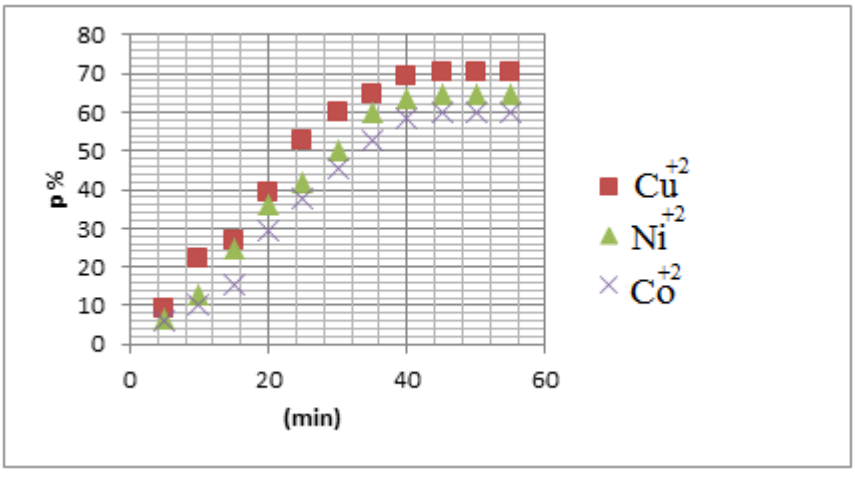


Figure (3) shows the changes in the percentage of extraction as a function of time using the ligand (I)

It can be concluded from the table and figure that after a time of 45 minutes the percentage of extraction remains constant and thus equilibrium is achieved.

5-2-1-2-A study of the effect of pH of the aqueous medium on the extraction process using the ligand (I):

The effect of medium acidity on the extraction process was studied by extracting 3×10^{-3} M concentrations of copper, cobalt, and nickel ions at fixed amounts of the ligand (I) at different pH values. Buffer solutions of ammonia and acetic acid were used, prepared by adding 100 ml of 0.1 M acetic acid gradually to a specific volume of 0.1 M ammonia until the desired pH was reached, followed by the addition of 5 ml of 0.1 M sodium chloride. The extraction process was repeated three times, and the average percentages were calculated, statistically analyzed, and ranked in the following table

Table (5) Effect of pH changes with constant concentration of ligand (I) and constant concentration of ions (II) in a dichloromethane solution.

n=3 a=0.95 $C_{ion}=1\times10^{-3}$ $C_{leg}=3\times10^{-3}$

P%			
Co^{+2}	Ni^{+2}	Cu^{+2}	pH
42.13	45.78	49	4
47.9	51.9	56	5
52.8	57.9	63.8	6
57.3	60.3	68.8	7
60	64.85	70	8
56.9	61.8	66.9	9
51.8	56.3	61.8	10
47.83	51.8	54.9	11
42.43	46.7	53.1	12

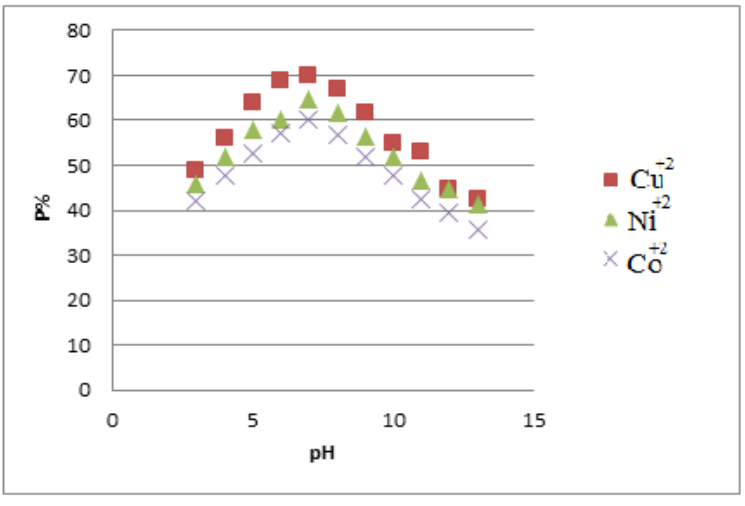


Figure (4) shows the percentage changes in extraction as a function of pH changes using the ligand (I).

It is observed from the table and figure that the percentage of extraction increases up to pH=7, then the extraction percentage decreases when the pH value increases. This is attributed to the fact that the nitrogen atom may become ferrous at a low pH and metal hydroxides are formed at high pH values.

5-2-1-3-Studying the effect of the solvent on the extraction process using the ligand (I):

The effect of using several solvents in the extraction process was studied by taking a concentration of 1×10-3 of (copper, nickel and cobalt(II)) ions with fixed amounts of the ligand (I) at a concentration of 3×10-3 at a pH value of 7. The extraction process was repeated three times and the average percentages were taken and statistically analyzed.

Table (6) Results of using more than one solvent on the extraction process using the ligand (I)

n=3 a=0.95 $C_{ion}=1\times10^{-3}$ $C_{leg}=3\times10^{-3}$ pH=7

P%			
Co^{+2}	Ni^{+2}	Cu^{+2}	solvent used
60.01	64.8	70	dichloromethane
59	63.01	69.7	chloroform
58.5	62.9	68	toluene

The results showed that the best solvent in the extraction process is dichloromethane, followed by chloroform and then toluene.

5-2-1-4-Studying the effect of using various salts of ions(II) on the extraction process using ligand(I):

The effect of using different mineral salts, such as chlorides, nitrates, and acets, in the extraction process was studied by taking a concentration of 1×10^{-3} of copper, cobalt, and nickel ions(II) with fixed amounts of the ligand (I) at a concentration of 3×10^{-3} at pH 7 in a dichloromethane solution. The extraction process was repeated three times, and the average percentages were calculated and statistically analyzed.

Table (7) Results of using more than one binary metal salt on the extraction process using the ligand (I).

n=3 a=0.95 $C_{ion}=1\times10^{-3}$ $C_{leg}=3\times10^{-3}$ pH=7

P%			
Co^{+2}	Ni^{+2}	Cu^{+2}	salt
60	64.89	70.1	chlorides
58.06	62	68	nitrates
56.92	58.87	66.9	acetates

The results showed a similarity in the extraction rate, and chlorides can be considered the best because they do not cause steric obstruction due to their small size compared to nitrates and acetates.

5-2-1-5-Studying the effect of changes in the ligand(I) concentration on the extraction process:

The effect of the concentration of the ligand (I) on the extraction process was studied by extracting certain quantities of (copper, nickel, cobalt) ions and increasing quantities of the hydrate (I) (0.25, 0.5, 0.75, 1) $10^{-3}\times$ mol/L in a solution of dichloromethane at pH=7. The changes in the logarithm of the extraction coefficient were studied in terms of the changes in the logarithm of the ligand concentration. The extraction process was repeated three times, and the average percentages of the three extraction processes were taken and statistically processed.

Table (8) Results of the process of extracting ions using different concentrations of the ligand (I).

n=3 a=0.95 $C_{ion}=1\times10^{-3}$ pH=7

Log(D) Co^{+2}	Log(D) Ni^{+2}	Log(D) Cu^{+2}	Log(I)	ligand concentration 10^{-3} *(I)
-0.257	-0.297	0.312	-3.60	0.25
-0.205	-0.0014	0.53	-3.30	0.5
-0.136	0.152	0.749	-3.12	0.75
-0.076	0.322	0.963	-3	1

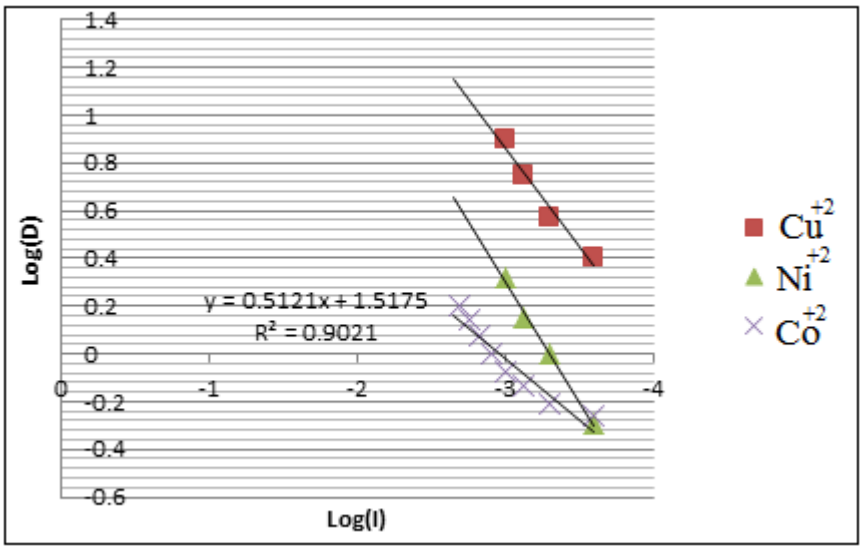


Figure (5) Changes in the logarithm of the metal ion extraction ions in terms of changes in the logarithm of the ligand(I) concentration .

From the previous figures, the slope is approximately 0.5, meaning the bonding ratio is (1:2) metal-bonded. The expected bonding sites are (P=S) and (N-H).

5-2-2- ligand(II):

5-2-2-1-Results of the study on the effect of shaking time on the extraction of ions(II) using the ligand(II):

Solutions of concentrations of 3×10^{-3} of the ligand(II) prepared in dichloromethane and aqueous solutions of divalent metal ions of concentration 3×10^{-3} at pH=8 were taken at laboratory temperature (25°C). The concentration of the ions extracted to the organic phase was determined, and the effect of time on the percentage of extraction was studied. The results were shown in the following table.

Table (9) Effect of mixing time on the extraction process of metal ions (II) using the ligand (II).

n=3 a=0.95 $C_{ion}=1\times10^{-3}$ $C_{leg}=3\times10^{-3}$ **pH=8**

P%			
Co^{+2}	Ni^{+2}	Cu^{+2}	time
39.4	39.5	45.7	5
34.6	45.7	51.65	10
39.54	51.65	57.8	15
45.7	58.9	62.87	20
51.27	63.8	69.87	25
59.8	66.43	76.3	30
64.2	67.9	78.31	35
65.5	68.23	78.32	40
65.5	68.23	78.32	45

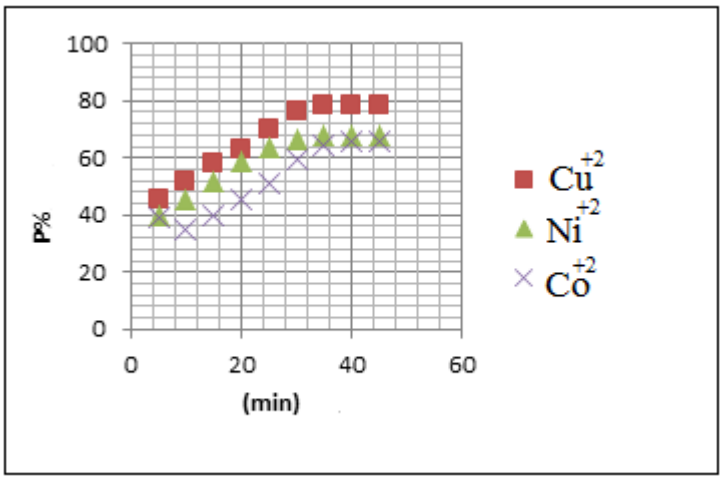


Figure (6) shows the changes in the percentage of extraction as a function of time using the ligand (II)

It can be concluded from the table and figure that after a time of 45 minutes the percentage of extraction remains constant for all ions used, and thus equilibrium is achieved.

5-2-2-2-A study of the effect of pH of the aqueous medium on the extraction process using the ligand (II):

The effect of medium acidity on the extraction process was studied by extracting 3×10^{-3} M concentrations of copper, cobalt, and nickel ions with fixed amounts of the **ligand** (II) group at a concentration of 3×10^{-3} M at different pH values. Buffer solutions of ammonia and acetic acid were used, prepared by taking 100 ml of 0.1 M acetic acid and gradually adding a specific volume of 0.1 M ammonia until the desired pH was reached, followed by the addition of 5 ml of 0.1 M sodium chloride. The extraction process was repeated three times, and the average percentages were calculated, statistically analyzed, and ranked in the following table

Table (10) Effect of pH changes with constant concentration of ligand (II) and constant concentration of ions (II) in a dichloromethane solution
n=3 a=0.95 $C_{ion}=1\times10^{-3}$ $C_{leg}=3\times10^{-3}$

P%			
Co^{+2}	Ni^{+2}	Cu^{+2}	pH
47.24	49.31	61.89	3
51.98	52.83	65.8	4
55.92	55.32	69.32	5
59.15	61.87	74.8	6
64.32	66.43	77.35	7
65.47	68.23	78.31	8
63	65.98	77.43	9
58.3	59.43	73.76	10

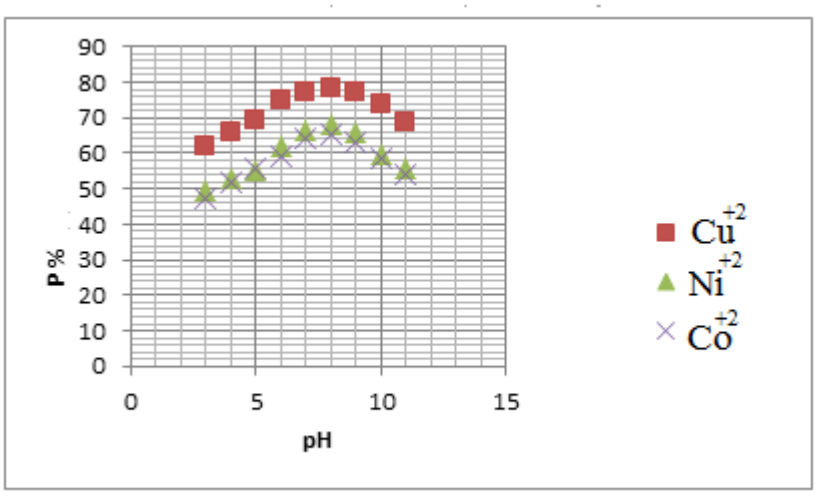


Figure (7) shows the percentage changes in extraction as a function of pH changes using the ligand (II).

It is observed from the table and figure that the percentage of extraction increases up to pH=8, then the extraction percentage decreases when the pH value increases. This is attributed to the fact that the nitrogen atom may become ferrous at a low pH and metal hydroxides are formed at a high pH.

5-2-1-4-Studying the effect of using various salts of ions(II) on the extraction process using ligand(II):

The effect of using several solvents in the extraction process was studied by taking a concentration of 1×10^{-3} of (copper, cobalt, nickel(II)) ions with fixed amounts of the **ligand** (II) at a concentration of 3×10-3 at a pH value of 8. The extraction process was repeated three times, and the average percentages were taken and statistically analyzed.

Table (11) Results of using more than one solvent on the extraction process using the ligand (II)

n=3 a=0.95 $C_{ion}=1\times10^{-3}$ $C_{leg}=3\times10^{-3}$ pH=8

P%			
Co^{+2}	Ni^{+2}	Cu^{+2}	solvent used
65.4	68.11	78.32	dichloromethane
63.8	65.7	77	chloroform
61.8	64.9	75	toluene

The results showed that the best solvent in the extraction process is dichloromethane, followed by chloroform and then toluene.

5-2-1-4-Studying the effect of changes in the ligand(I) concentration on the extraction process:

The effect of the concentration of the ligand (II) on the extraction process was studied by extracting certain quantities of (copper, nickel, cobalt) ions and increasing quantities of the hydrate (I) (0.25, 0.5, 0.75, 1) $10^{-3}\times$ mol/L in a solution of dichloromethane at pH=8. The changes in the logarithm of the extraction coefficient were studied in terms of the changes in the logarithm of the concentration of the ligand (II). The extraction process was repeated three times, and the average percentages of the three extraction processes were taken and statistically processed.

Table (12) Results of the process of extracting ions using different concentrations of the ligand (II)

n=3 a=0.95 $C_{ion}=1\times10^{-3}$ pH=8

Log(D) Co^{+2}	Log(D) Ni^{+2}	Log(D)Cu^{+2}	Log[II]	concentrations of the ligand (II)*10^{-3}

0.03	0.04	0.08	-3.602	0.25
0.12	0.123	0.162	-3.301	0.5
0.24	0.25	0.26	-3.124	0.75
0.33	0.39	0.4	-3	1

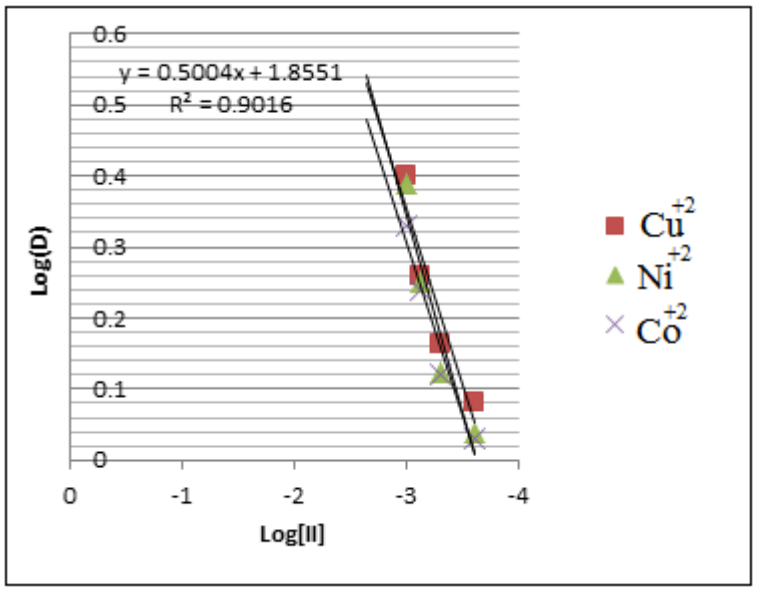


Figure (8) Changes in the logarithm of the metal ion extraction ions in terms of changes in the logarithm of the ligand(II) concentration .

From the previous figures, the affinity is approximately 0.5 for all ions, meaning the bonding ratio is (1:2) bonded: metal. The expected bonding sites are (P=S) and (N-H).

6-Conclusions and Recommendations:

6-1- Conclusions :

1- The two related compounds (I) and (II) P,P,N tri pheny lphosphene thioic amide and O,O diphenyl-phenylphosphoramide thiotre are new derivatives of organophosphorus compounds.
2-It is concluded from studying the spectra that the ligands obtained are identical to the structure of the compounds proposed for preparation.
3-The optimal extraction time is 45 minutes in order to achieve a balance between the aqueous and organic phases.
4-The ligand(II) shows a greater ability to extract metal ions(II) than the ligand(I) because it contains a P-O bond that helps in the extraction process
5-The best extraction occurs at a pH value of 7 for the ligand (I) and pH value of 8 for the ligand (II). This is attributed to the fact that the nitrogen atom may be nitrified at a low pH and metal hydroxides are formed at a high pH.
6-It is concluded from studying the change in the logarithm of the distribution factors with the change in the logarithm of the concentration of the ligands that the ligand-metal ratio is (1:2).
7-Dichloromethane solvent has a greater extraction capacity than chloroform and toluene due to its dielectric constant, as the blocking constants are as follows: Dichloromethane 9.1 > Chloroform 4.81 > Toluene 2.38.
8-By comparing the extraction results, we find that the highest extraction rate is due to copper ions, followed by nickel and then cobalt. This is explained based on the difference in the radii of the metal ions used, and they are arranged according to increasing radius as follows: $Cu^{+2}<Ni^{+2}<Co^{+2}$, since the ability of

the ligand to chelate and extract the ion increases as the radius of the ion to be extracted is smaller, and they form more stable complexes.

6-2-Recommendations:

1-The extraction process using these compounds can be applied more broadly with other metal ions.
2-Studying other factors that affect the extraction process, such as temperature.
3-Using the two ligands to obtain complexes for some metal ions.
4-Studying some other thermodynamic functions.

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