J. Chem. Soc. Nigeria, Vol. 40, No.2, pp 6-14 [2015]

EXTRACTIVE DETERMINATION OF Zn(II) AND Cd(II) IN INDUSTRIAL SAMPLES USING 1, 5-DIMETHYL-2-PHENYL-4[(E)-2,3,4- TRIHYDROXY PHENYL)]DIAZENYL-1,2-DIHYDROXYL-3H-PYRAZOL-3-ONE, (H_3L).

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Accepted:18/07/2015
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Abstract
H_3L was synthesized by coupling diazotized 4- aminoantipyrene with 1, 2, 3,-trihydroxybenzene. It coordinated as a tetradentate ligand to Zn(II) and Cd(II) to form $[Zn(H_2L)_2]$ and $[Cd(H_2L)_2]$ respectively. The ligand was characterized by ^1H and ^{13}C NMR, Infrared and UV spectroscopy whereas the complexes were characterized via UV and IR spectroscopy as well as conductivity and mole ratio determinations. Extractive determinations were based on the formation of darkbrown hydrophilic complexes of Zn(II) and Cd(II) by H_3L, which are readily extractible into chloroform. Effects of extraction variables like pH, salting –out agents, masking agents and concentration of H^+ was studied. Cd(II) was quantitatively extracted in 0.001M HCl up to 100% but masked by 0.001M of either SCN^- or tartrate up to 90% under five minutes. Extraction of Zn(II) with $H_3L/CHCl_3$ was also quantitative(96%) in 0.001M HCl within 70 min, but was masked by CN^- and SCN^- up to 79% and 67% respectively. Cd(II) was successfully separated from Zn(II) in a four cycle extraction in 0.001M HCl using $H_3L/CHCl_3$ in the presence of 1M CN^-. Recovery of Zn(II) and Cd(II) from rubber carpet following the procedure reached 90% and 85% respectively.

Keywords: 1, 5- Dimethyl-2-phenyl-4[(E)-2,3,4- trihydroxyphenyl)]diazenyl-1,2-dihydroxyl-3H-pyrazol-3-one, (H_3L), extractive determination of Zn(II) and Cd(II).

Introduction

Azo compounds have a great biological activity[1-4] as well as industrial importance[5]. Azo pyrazole derivatives and its metal complexes have been used for dying papers due to its fastness property[6] and possess high dying power on fibres[7]. They have been applied for the solvent extraction of metals ions [8, 9], for analytical purposes[10], in the production of azo colourants[11], as ligands in complexes with catalytic activity[12] and in rare earth metal complexes with interesting photophysical properties[13].

1,5-dimethyl-2-phenyl-4-[(E)-(2,3,4-trihydroxyl phenyl)diazenyl]-1,2-dihydro-3H-pyrazol-3-one,(H_3L) has been synthesized and its coordination properties with respect to Co(II), Fe(III), and Os(VIII), as well as its biological activities has been reported[14]. Recently, its extraction with respect to Co(II) and Fe(III) has been investigated using H_3L in organic diluent[9]. In the report, dichloroethane / H_3L extracted Fe(III) up to 96.25% in 0.001 M $HClO_4$ medium, and EDTA masked Fe(III) up to 77.75% within 5 min. Also chloroform / H_3L extracted Co(II) up to 81.2% in 0.001 M H_2SO_4 within 10 min. Moreover, Fe(III) was successfully separated from Co(II) by four cycle extraction at pH 6 using H_3L at 0.1M EDTA.

Zinc and cadmium belongs to group 12 in the periodic table. Zinc occurs as ore in zinc sphalerite, marmatite [(Zn,Fe)S] and calamine or smithsonite ($ZnCO_3$). Cadmium on the other hand, occurs in a few minerals and in small quantities in other ores especially zinc ore, from which it is produced as a by-product. Zinc is used in the corrosion protection of iron and steel; brass alloys, cast-zinc alloys, wrought alloys and in miscellaneous uses such as chemicals and zinc dust[15]. In industry, it is used as a reducing agent, manganese dioxide primary batteries and in metallurgical industry as a cementation agent[15]. While cadmuim is mostly used in electroplating onto steel, iron, copper, brass and other alloys to protect them from rusting, as anode material in rechargeable storage batteries in which the oxide of nickel or silver is the cathode [16].

Zinc ores are recovered by mining techniques (most commonly used is cut-and-fill stopping); its extraction entails the process of electrolysis; and using zinc-lead blast furnace process; and refining by distillation[15]. Cadmium can be recovered from fumes eliminated during the sintering of zinc concentrates, from the dust collected from the gases leaving lead blast furnace, and from various residues produced during the electrolytic refining of zinc [17]. Looking at the above extraction methodologies, there is a need, to adopt a method that is cheaper, and easier with a high yield of cadmium and zinc. That is why, this work reports the use of H_3L/chloroform to extract Zn(II) and Cd(II) ions from aqueous solution; to separate Cd(II) from Zn(II); and to extract Cd(II) and Zn(II) ions from industrial material.

Materials and Methods

All the reagents used were of analytical grade and were used as supplied without further purification. The electronic absorption spectra were recorded in ethanol on UV- 2500 PC Spectrophotometer. The FTIR spectra were performed using FTIR – 8400S Spectrophotometer (SHIMADZU) at the National Research Institute for Chemical Technology(NARICT) Zaria Kaduna state in the range 4500 – 200 cm^{-1} using KBr. The ^{1}H and ^{13}C NMR spectra were recorded in DMSO using 200Varian NMR Spectrophotometer. The conductivity measurement were made in methanol using WTW LF90 conductivity meter. Melting points were determined using Fisher Johns melting point apparatus and were uncorrected. Absorbance measurements were taken using JENWAY 6305S Spectrophotometer.

Buffer solutions of pH 1-13 were prepared following Clarks and Lubbs method[18]. The pH of the solutions was confirmed using a pH meter. Stoichiometry of the complexes were determined by employing Job's continuous variation of analysis[19].

Synthesis of 1, 5- dimethyl-2-phenyl-4[(e)-2,3,4-trihydroxyphenyl)]diazenyl-1,2-dihydroxyl-3h-pyrazol-3-one, (H_3L)

H_3L was prepared following the method given by Heinosuke Yasuda[20]. A solution of 4-aminoantipyrene (1.015 g, 10 mmole) was dissolved in dilute hydrochloric acid (25mL) and diazotized with sodium nitrite solution (0.69 g, 10 mmole) below 5 ^{0}C with hand stirring. The resulting diazotized 4-aminoantipyrine was poured into a mixture of 1, 2, 3, -trihydroxylbenzene(0.63g, 10 mmole) and sodium acetate solution (1.00M) using mechanical stirring at room temperature. The brown coloured product separated out, was collected by filteration and washed with methanol/water (1:5). The compound was recrystallized from 1:1 methanol/ dichloromethane solution and stored in a dessicator over $CaCl_2$. The yield was 35.4%, melting point of 190 ^{0}C and conductivity value of 0. 00 $\Omega^{-1}cm^2\ mol^{-1}$.

Synthesis of $[Zn(H_2L)_2]$ and$[Cd(H_2L)_2]$

The complexes were synthesized by refluxing ethanol solutions of $ZnCl_2$ and $CdCl_2$ with the ligand respectively in amounts equal to metal: ligand molar ratio of 1: 2 in accordance to the method given by El.saied et al[21]. To ethanolic solution (50 mL) of $ZnCl_2$ (0.001 mole, 0.135g) was added a solution of H_3L (0.002mole, 0.68g) in ethanol (40 mL). The mixture was refluxed for 6 h under constant stirring at 60 ^{0}C. On cooling, a dark brown coloured precipitate formed. The resulting solid was filtered off, recrystallized from methanol and stored in a desiccator over $CaCl_2$. The yield was 99 %, melting point 290 ^{0}C and conductivity value of 8.9 $\Omega^{-1}cm^2mol^{-1}$.

The same procedure was repeated using $CdCl_2$ (0.001mole, 0.182g). A dark brown precipitate was formed; yield was 78 %, melting point of 220 ^{0}C and conductivity value of 9.1 $\Omega^{-1}cm^2\ mol^{-1}$.

Stoichiometric Determination

A 10^{-3}M solution of the ligand and metal salts were prepared in ethanol. Varying volumes of the metal salt solution were mixed with various volumes of the ligand such that the total volume of the mixture at each run equals 5 mL. These mixtures were corked, shaken and allowed to stand and react for 30 min before taking their absorbance at a 435nm and 439nm for Zn and Cd complexes respectively.

Extraction Procedure

Equilibration Temperature: Solution of both organic and aqueous phases were allowed to equilibrate at room temperature (27±1 °C) before mixing for extraction; and all extractions were carried out at room temperature.

Equilibration time

Solution of metal ion under study was pipetted (0.6 mL, of 10 µg/ mL) into different extraction bottles, and each was made up to 6 mL with deionised water.

An $8x10^{-3}$% $H_3L/CHCl_3$ solution was prepared. Equal volumes (6 mL) of this solution were added into the aqueous phase; one bottle removed at a time after a desired time interval of 5, 10, 20, 40, 60, and 70 min. The two phases were centrifuged and separated. The amount of metal ion left unextracted in the aqueous phase was determined using the method given for spectrophotometric analysis of Cd(II) ions [22] and Zn(II) ions [23] respectively.

Extraction from Buffer Solution

Exactly 0.6 mL of 10 µg/mL solution of metal ion under study was pipetted, into different extraction bottles, representing pH values from 1 to 13 and was made up to 6 mL with the corresponding buffer solution.

An $8x10^{-3}$% $H_3L/CHCl_3$ solution was prepared. Equal volumes (6 mL) of this solution were added into the aqueous phase in the extraction bottles. The phases were equilibrated based on the appropriate time, centrifuged and separated. The amount of unextracted metal ion was determined using the method given for spectrophotometric analysis of Cd(II) ions [22] and Zn(II) ions [23] respectively.

Extraction from Acid Media

Solution of metal ion under study was pipetted (0.6 mL of 10µg/mL) into different extraction bottles. From 2M solutions of the acid used (H_2SO_4, HCl, HNO_3 and $HClO_4$), 0.003mL, 0.03 mL, 0.3mL, and 3mL were pipetted into the extraction bottles respectively. Hence, on final dilution to 6 mL with deionized water, concentration range of 0.001M to 1M was obtained. An $8x10^{-3}$% $H_3L/CHCl_3$ solution was prepared. Equal volumes (6 mL) of this solution were added into the aqueous phase in the extraction bottles. The phases were equilibrated based on the appropriate time, centrifuged and separated. The amount of unextracted metal ion was determined using the

method given for spectrophotometric analysis of Cd(II) ions [22] and Zn(II) ions [23] respectively.

Extraction in salting-Out Agent

From 2M solutions of Na_2SO_4, NaCl, KNO_3, and $KClO_3$, 0.003mL, 0.03 mL, 0.3mL, and 3mL were pipetted into the extraction bottles respectively such that on dilution to 6 mL with deionized water, concentration range of 0.001M to 1M was obtained. The concentration of the corresponding acids (H_2SO_4, HCl, HNO_3 or $HClO_4$) where there is least extraction of the metal ions was determined from the plot of percentage extraction against acid concentration. The volume of acid that corresponds to these acid concentrations was added into the extraction bottles. An $8x10^{-3}$% $H_3L/CHCl_3$ solution was prepared. Equal volumes (6 mL) of this solution were added into the aqueous phase in the extraction bottles. The phases were equilibrated based on the appropriate time, centrifuged and separated. The amount of unextracted metal ion was determined using the method given for spectrophotometric analysis of Cd(II) ions [22] and Zn(II) ions [23] respectively.

Extraction in Complexing Agent

Following the extraction procedure, cyanide, oxalate, EDTA, thiocyanate, tartrate or phthalate were added separately to the extraction mixtures to cover the concentration range of 0.001 to 1 M, in 6 mL of final solution. Volume of acid that allows for quantitative extraction was determined from the graph and added. An $8x10^{-3}$% $H_3L/CHCl_3$ solution was prepared. Equal volumes (6 mL) of this solution were added into the aqueous phase in the extraction bottles. The phases were equilibrated based on the appropriate time, centrifuged and separated. The amount of unextracted metal ion was determined using the method given for spectrophotometric analysis of Cd(II) ions [22] and Zn(II) ions [23] respectively.

Measurement of Distribution ratio

After separation of the two phases, the amount of metal unextracted in the aqueous phase and the amount of metal extracted in organic phase was analysed spectrophotometrically. The distribution ratio of the metal was calculated as the ratio of the concentration of the metal ion in the organic phase to that in the aqueous phase.

Spectrophotometric Analysis of the metal ions

For Cadmium (II)

A 0.4 mL of 25% sodium tartrate, 2 mL of (a mixture of 40% NaOH and 1% KCN) and 0.4 mL of 20% hydroxylamine hydrochloride was added to a slightly acidic cadmium (II) raffinates. The mixture was shaken in a separating bottle for two minutes with 6 mL of 0.001% dithizone in chloroform. The phases were allowed to separate out and absorbance of the organic layer was recorded at 518 nm[23]. Chloroform was used as blank.

For Zinc (II) A 5 mL buffer solution (pH 4.75, a mixture of equal volume of 2M sodium acetate and 2M acetic acid in the ratio of 1:1) and 1 mL of 25% sodium thiosulphate solution was added to 10 mL slightly aqueous zinc(II) extraction raffinate. The mixture was vigorously shaken for 2 min with 5 mL of 0.001% dithizone in carbon tetrachloride. The absorbance of the organic layer was determined at 540 nm[24]. Carbon tetrachloride was used as blank.

Calibration Curve

Aliquots of the metal ion solutions, which was made slightly acidic with dilute HCl was pipetted into separate extraction bottles such that on final dilution to 10 mL , the concentration range of 0.1- 1.0 ug/ mL was obtained. The metal ion solution was treated as outlined above and the absorbance measured at 518 nm for Cd(II) ions and at 540 nm for Zn(II) ions. The concentration of each metal ion after extraction was read from the straight line graph using absorbance obtained.

Separation of Metal Solution

A mixture of equal amount (2ug/mL) of Cd(II) and Zn(II) in 0.001 M of HCl and containing 1M cyanide solution was made up to 5 mL using deionized water, Cadmium(II) was extracted with equal volume (5 mL) of 8 $x10^{-3}$ % $H_3L/CHCl_3$; for the extraction time of Cd(II) the phases were centrifuged, allowed to settle, and separated. The extraction was repeated three[24] times with fresh reagent solution. The aqueous and the combined organic extract were analysed spectrophotometrically for both metals as stated above.

Following the extraction procedure, cadmium (II) was separated from zinc(II) in 0.001 M of HCl, and containing 1 M cyanide solution.

Extraction from the Industrial Material

Rubber carpet (1 mm thick) was purchased from Ogige market in Nsukka. Solution of this material was used to extract zinc (II) and cadmium (II) ions. A sample of the ground rubber carpet, was dried in an oven at 80 $^{\circ}C$ for 12 h, and later kept in a dessicator[25]. The sample was prepared following the method given by Elinder et al[26]. Exactly 2.3 g of the sample was ashed in a muffle furnance at 450 ^{0}C, then 0.4 g of the ashed sample was treated with 5 mL of conc. HNO_3 and was evaporated to almost dryness. The sample was dissolved with 1 M HNO_3.The solution was filtered with 40% Whatmann filter paper into a volumetric flask and was made up to mark with distilled water. Exactly 1 mL aliquot of the solution was pipetted, into an extraction bottle. For determination of Cd(II) ions, 1 M CN^- with 0.001 M of HCl was added and made up to 5 mL with deionised water. For determination of Zn(II), 1 M tartrate with 0.001 M HCl was added to 1 mL of the carpet solution, and was made up to 5 mL with deionised water.

Equal amount (5 mL) of $8x10^{-3}$ % $H_3L/ CHCl_3$ (W/V) was added into the extraction bottles. The phases were equilibrated based on the appropriate time for the metal, centrifuged and separated out. The extraction was repeated three[25] more times with fresh 5 mL

reagent solution from organic solution. The amount of metal ion left unextracted in the aqueous phase was determined as outlined above [22, 23].

Results and Discussion

H_3L was synthesized as shown in Scheme 1. It was subsequently used to prepare $[Zn(H_2L)_{2]}$ and $[Cd(H_2L)_2]$. All the synthesized compounds are air stable, powdery and non- hygroscopic with high melting points. They are soluble in dimethyl formamide and chloroform but insoluble in hexane. Physical data of the synthesized compounds are tabulated in Table 1. The molar conductivities of the complexes are in the range 8.9 – 9.1 $\Omega^{-1}cm^2\ mol^{-1}$ in DMSO, suggesting that the complexes are non-electrolytes in DMSO-[27 -29]. Jobs continuous variation gave a 1:2 metal to ligand stoichiometry for both complexes.

Electronic Spectra

T he electronic absorption spectra of H_3L and its complexes are shown in Table 2. H_3L showed strong absorptions at 209, 249 and 278 nm and an absorption of relatively weak intensity at 376 nm. These have been assigned to $\pi - \pi^*$ transitions of the conjugated π bonds and $n - \pi^*$ transitions of the non- bonding electrons in the ligand. $[Zn(H_2L)_2]$ and$[Cd(H_2L)_2]$ chelates are diamagnetic with d^{10} configuration and their electronic spectra exhibited bands in the range 25510 – 1361cm^{-1}. These absorptions have been assigned to charge transfer transitions[30].

Infrared Spectra

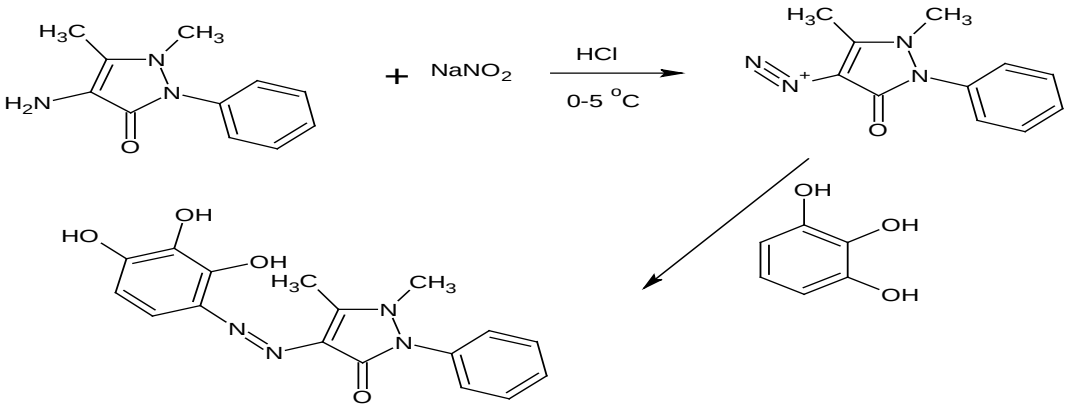
The IR data of the ligand and complexes are listed in Table 3. Comparison of the IR spectra of the H_3L, Zn and Cd complexes show broad bands at 3249, 3420 and 3412cm^{-1} respectively due to ν (O-H). The (O-H) vibrations increased by 171 – 163 cm^{-1} on complexation and suggests deprotonation of the phenolic O-H prior to ligation[33, 34]. The absorption bands in the range 1620- 1604cm^{-1} was assigned to ν (C=O), although it appeared relatively low. A 16-12cm^{-1} frequency lowering was observed in the complexes showing involvement of C=O in coordination[30]. The (N=N) vibration for H_3L, Zn(II) and Cd(II) complexes were observed as a strong band at 1406, 1419, 1417cm^{-1} respectively. A 11-13 cm^{-1} frequency increase was observed in ν (N=N) of the complexes compared with the value for H_3L, indicating coordination of an N=N group to the metals, a result which is further substantiated by the appearance of bands in the 400-449 cm^{-1} region assignable to ν (M-N)[32, 35]. In the complexes bands assigned to vibration frequency of the phenolic C-O undergo positive shift indicating that the ligand is bonded to the metallic ions through the phenolic oxygen atoms[30 - 35].

Table 1: Physical properties of H_3L, $[Zn(H_2L)_2]$ and $[Cd(H_2L)_2]$

Compounds	Colour	Texture	Melting point(0 C)	MW (g/mol)	$\Omega^{-1}cm^2\ mol^{-1}$	% yield
H_3L	Brown	powdery	190	340	0.00	35.4
$[Zn(H_2L)_2]$	Dark brown	Powdery	290	740	8.9	99
$[Cd(H_2L)_2]$	Dark brown	Powdery	220	787	9.1	78

Table 2: Electronic spectral data of H_3L, $[Zn(H_2L)_2]$ and $[Cd(H_2L)_2]$

Compound	Wavelength (nm)	Wavelength (cm^{-1})	Assignment
H_3L	209	47846	$\pi - \pi^*$
	249	40160	$\pi - \pi^*$
	278	35911	$\pi - \pi^*$
	376	26595	$n - \pi^*$
$[Zn(H_2L)_2]$	392	25510	Charge transfer
	435	22988	Charge transfer
	735	13605	Charge transfer
$[Cd(H_2L)_2]$	439	22753	Charge transfer
	733	13642	Charge transfer



Scheme 1: Synthesis of H_3L

Table 3: Infrared spectral data of H_3L, $[Zn(H_2L)_2]$ and $[Cd(H_2L)_2]$

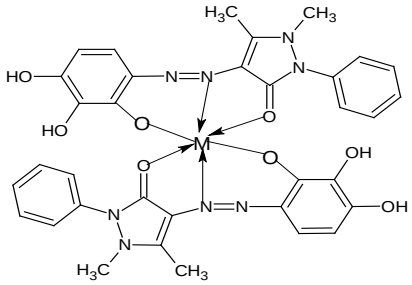
Compd.	ν(O-H)	ν (C-H)	ν (C=O)	ν (C=C)	ν (N=N)	ν (C-O)	ν (M –O)	ν (M-N)
H_3L	3249	-	1620	1498	1406	1319	-	-
$[Zn(H_2L)_2]$	3420	2951	1608	1507	1419	1335	525	400
$[Cd(H_2L)_2]$	3412	2938	1604	1508	1417	1335	505	449

^{1}H and ^{13}C NMR spectra

H_3L showed a singlet peak at 2.42(3H, s) and 3.22(3H, s) assigned to methyl protons. Doublet peaks at 6.41(1H, s) and 7.02(1H, d) were assigned to protons on trihydroxyphenyl ring. The signal at 7.42 ppm(5H,m) was assigned to phenyl protons.

The ^{13}C NMR for H_3L gave 13 peaks which corresponded to the 13 different carbons present in the compound. The ^{13}C NMR spectra of the H_3L and the structure showing carbon numbering is given in Table4. The peak at 159.07 ppm was assigned to carbonyl carbon since it is the most deshielded[36].

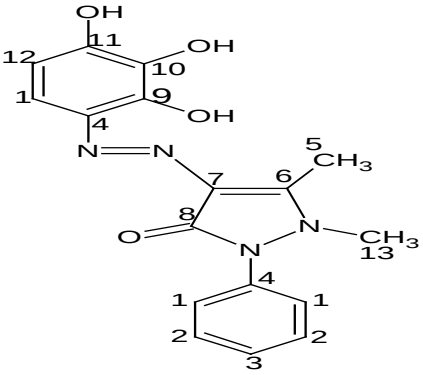
Based on the UV, IR and NMR spectral studies, octahedral geometry was proposed for Zinc (II) and Cadmium(II) complexes.



M = Zn, Cd

Fig. 1: Proposed structure of the metal complexes

Table 4: ^{13}C NMR spectral data (ppm) OF H_3L

Position of Carbon	^{13}C NMR Value	Structure showing carbon numbering
C1	120.80	
C2	130.02	
C3	128.74	
C4	133.39	
C5	108.23	
C6	134.60	
C7	143.43	
C8	159.07	
C9	149.28	
C10	147.53	
C11	143.53	
C12	133.57	
C13	119.62	

Equilibration time

The equilibration time required for the extraction of zinc(II) and cadmium(II) with 8 x 10^{-3}% of ligand in chloroform as seen in Table 5 is 70min and 5min respectively.

Table 5: Quantity of Zn(ii) and Cd(ii) extracted into organic phase at different time intervals (metal ion concentration 1µg/cm^3 in aqueous phase)

Time(min)	Zn(II) in organic phase(µg/ml)	Cd(II) in organic phase(µg/ml)
5	0.080	0.760
10	0.010	0.500
20	0.470	0.620
40	0.520	0.690
60	0.650	0.680
70	0.840	0.460

The Effect of pH on extraction of Zn(II) And Cd(II) ions.

Studies on extraction of Zn (II) ions showed low percentage extraction between pH 8 and 1. This may be due to competition between H^+ and Zn^{2+} for the azo-nitrogen ligation sites, which was unfavourable for the formation of the complex. At pH 9, the percentage extraction was up to 65%. This could be attributed to the formation of a neutral chelate complex for optimium extraction into organic phase. As pH increased to 13, the percentage extraction decreased, which may be due to hydrolysis of the metal ion and masking effect of base component of buffer. Studies on extraction of Cd(II) ions indicated low extraction between pH 12 and 1. This may be due to high competition between protons and Cd(II) ions for the azo-nitrogen ligation sites which was unfavourable for the formation of the complex. At pH 12, the percentage extraction of Cd(II) ions was 45%. This may be due to the oxidation state of Cd(II) and the masking effect from components of the buffer solution. As pH increases to 13, the percentage extraction decreases. This may be attributed to hydrolysis of Cd(II) ions at high pH, thus decreasing the amount available for bonding.

Effect of acidity on extraction

For Zn (II), in H_2SO_4, HCl and $HClO_4$, there was an increase in percentage extraction at low concentration. While in HNO_3, increase in percentage extraction was observed at high concentration. For Cd(II), in HNO_3, HCl and $HClO_4$, increase in percentage extraction was observed at low acid concentration. While in H_2SO_4, increase in percentage extraction was observed at high concentration. Increase in percentage extraction at low concentration suggests that deprotonation of H_3L was favoured, enhancing the formation of the complex. As the acid concentration increases to 1M, the percentage extraction decreased, which may be due to competition for the azo-nitrogen ligation sites between the protons and the ions.

Effect of salting-out agent on extraction

It was observed that 0.001M NaCl, 0.001M KNO_3 and 1M of Na_2SO_4 enhances increase in percentage extraction up to 87%, 74% and 94% respectively for extraction of Zn(II) ions. This may be attributed to increase in dielectric constant of the aqueous media, which makes the complex less ionic, hence more soluble in the organic phase [10]. As concentration increases to 1 M, the amount extracted decreased. This could be attributed to decrease in dielectric constant. For $KClO_4$; there was a general decrease in percentage extraction in all concentrations, this may be due to formation of more un-extractable $Zn(ClO_4)_2$, masking the extractability of the compex. There were increased in percentage extraction of Cd(II) ions in 1M NaCl, 0.001 M Na_2SO_4, 1 M KNO_3 and 0.001M $KClO_4$. This suggests that the ionic activities of extractable metal chelate were decreased, leading to increase in percentage extraction. It may also be attributed to an increase in dielectric constant of the aqueous media that makes the complex less ionic, hence more soluble in the organic phase than in aqueous phase.

Effect of masking agent on Extraction

It was observed that cyanide has the highest masking effect on Zn(II), followed by oxalate; next was thiocyanate, tatrate, EDTA, and finally phthalate. Cyanide, has the highest masking effect at 1 M concentration (up to 79%). That is to say, addition of cyanide in aqueous phase, formed complex with the zinc ion thereby, competing with the chelating agent and lowered the distribution ratio. Also, 0.001 M oxalate, masked 69%; 1 M thiocyanate masked up to 67%; 1 M EDTA interfere the extraction up to 57%. Exactly 0.001 M tatrate masked 61%; and M phthalate masked 56%. For Cd(II); it was observed that 0.001 M thiocyanate and 0.001 M tatrate, masked up to 90 %, these were followed by 1 M oxalate 77%; 0.001 M cyanide and 0.001 M EDTA masked up to 65 % and 63 % respectively. Phthalate (1M) that has the least masking effect, interfered up to 46%. Generally, the masking agents here formed water-soluble complexes with the Cd(II) ions in competition with the extracting agent.

Metal Separation

Table 6 shows the results obtained in separating Cd(II) from Zn(II) ion, using 1 M cyanide in 0.001M HCl using 8 x 10^{-3} µg/cm^3 $H_3L/CHCl_3$. This condition was based on the fact that Cd(II) ions is quantitatively extracted in 0.001M HCl and that 1M cyanide only masked 19% of cadmium(II) within five minutes, where as up to 79% of zinc(II) can be masked for seventy minutes. Therefore, it was possible to separate the two metals via a four-cycle extraction process to increase the percentage yield. The results obtained were as follows:

Table 6: The results obtained from separation of Cd(II) from Zn(II)		
Element	Amount taken (µg/ml) aqueous phase	Amount found (µg/ml) aqueous phase
Zn(II)	2.0 2.0	2.00 1.98 1.96 1.91
Cd(II)	2.0	0.31 0.18 0.12 0.07

Determination of Metal from Industrial Material

The concentration of Cd(II) and Zn(II) ions in the rubber carpet solution was determined using AAS. The result gave 0.1µg/ml for Cd(II) ions and 5.84µg/ml for Zn(II) ions. From 5.84µg/ml, 1.5µg/ml was used for extraction. Therefore, the two metals were separately extracted from rubber carpet solution via a four-cycle extraction process. The result obtained is shown in Table 7. The recovery of Zn(II) and Cd(II) was up to 90% and 85% respectively under the established parameters

Table 7: Results obtained from metal extracted		
from real samples. Element	Amount taken (µg/ml) (aqueous phase)	Amount found (µg/ml) (aqueous phase)
Zn(II)	1.5	0.69 0.56 0.42 0.15
Cd(II)	0.1	0.073 0.065 0.035 0.015

Table 8: Extraction constants of the metal ions				
Metal	Slope(n)	Intercept	Conc. of ligand [HA]	K_{ex}
Zn(II)	0.141	-1.160	$8x10^{-3}$	7.316
Cd(II)	0.0516	-0.744	$8x10^{-3}$	3.899

Quantitative Treatment of Solvent Extraction

Quantitative treatment of extraction was calculated using the equation: Log D = nlog[HA] + npH + $logK_{ex}$. A graph of log D as plotted against pH. The slope equals n, intercept: $logK_{ex}$ + nlog [HA], and [HA] is the concentration of the ligand (H_3L) used (which was kept constant).The result obtained is shown in Table 8.

Conclusion

H_3L; and $Zn(H_2L)_2$ and $Cd(H_2L)_2$ complexes were successfully synthesized. Metal – ligand mole ratio indicated 1: 2 for the two complexes.

Solvent extraction studies were carried out on both zinc(II) and cadmium(II) ions using the ligand (H_3L), under different conditions. The effect of pH, acidic medium, salting-out and masking agent were studied. Cd(II) was quantitatively extracted in 0.001M HCl up to 100% but masked by 0.001M of either SCN^- or tartrate up to 90% under five minutes. Extraction of Zn(II) with $H_3L/CHCl_3$ was also quantitative(96%) in 0.001M HCl within 70 min, but was masked by CN^- and SCN^- up to 79% and 67% respectively. Cd(II) was successfully separated from Zn(II) in a four cycle extraction in 0.001M HCl using $H_3L/CHCl_3$ in the presence of 1M CN^-. Recovery of Zn(II) and Cd(II) from rubber carpet following the procedure reached 90% and 85% respectively.

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