STUDIES ON EXTRACTION OF Co (II) IONS FROM AQUEOUS SOLUTION USING 1,5-DIMETHYL-2-PHENYL-4-[(E)-(2,3,4-TRIHYDROXYLPHENYL)DIAZENYL]-1,2-DIHYDRO-3H-PYRAZOL-3-ONE

P.O Ukoha, *N R Ekere and I J Opara
Department of Pure & Industrial Chemistry, University of Nigeria, Nsukka, Nigeria
*corresponding author:nwachukwu64@gmail.com

Abstract
Solvent extraction studies on Co(II) using 1,5-dimethyl-2-phenyl-4-[(E)-(2,3,4-trihydroxylphenyl)diazenyl]-1,2-dihydro-3H-pyrazol-3-one (H$_3$L) were carried out using CHCl$_3$ as solvent. The ligand 1,5-dimethyl-2-phenyl-4-[(E)-(2,3,4-trihydroxylphenyl)diazenyl]-1,2-dihydro-3H-pyrazol-3-one (H$_3$L) and its Co(II) complex were successfully synthesized and authenticated. Stoichiometric studies indicated that the complex formed by Co(II) with H$_3$L have 2:1 ligand to metal mole ratio. The conductivity test on the ligand and its complex showed that H$_3$L and [Co (H$_2$L)$_2$] are non-electrolytes. Effects of some extraction variables like pH, salting out agents, time and acids were also investigated. Extraction of Co (II) with H$_3$L/CHCl$_3$ was quantitative (91.66%) at pH 10. Also in 10$^{-3}$ M H$_2$SO$_4$, Co (II) was extracted up to 81.2% within ten minutes. The result showed that the amount extracted decreased with increase in acid concentration. Na$_2$SO$_4$ and KClO$_4$ proved to be good salting out agents for the extraction of Co (II). The ligand synthesised has high potentials for removal of Co (II) from samples.

Keywords: Extraction; cobalt; ligand; H$_3$L; azo; complexation; spectrophotometry.

Introduction
Solvent extraction has made a lot of progress in the separation of metal cations since the discovery of organic chelating ligands and diluents that replaced explosive ones. For example Fisher discovered dithizone in chloroform or carbon tetrachloride with effective control of pH of the solution one can extract as many as six metals. This was followed by the discovery of cupferron an ideal reagent for both iron (III) and copper(II) at varying condition of extraction. Sandell and his group discovered dimethyl-glyoxime which was a real land mark in the chemistry of organic ligands. Dimethyl-glyoxime is used for the complexation of nickel, palladium and bismuth. The basic requirement for a solute to be extractable from an aqueous solution is that it should be uncharged or can form part of an uncharged ionic aggregate. Charge neutrality reduces electrostatic interactions between solute and water and hence lowers its aqueous solubility. Before extraction, the metal ion in the aqueous solution is in the form of metal-aquo complex while the organic phase consist of the organic chelating agent. The chelating agent converts the metal-aquo complex into a neutral metal chelate that distributes itself between the two liquid phases in definite ratio. Solvent extraction of metals has been extensively used in hydrometallurgical operations and more recently in the treatment of waste water to remove soluble metals. Because salts are usually not soluble in organic solvents, the extraction process require the introduction of an extractant that will combine with the metal ion to form an organic soluble species.

Most of the general types of compound available as extractants are dicarboxylic acids, aliphatic amines, aromatic amines, amino acids and hydroxyl acids. The extraction capacity and selectivity of extractants depends on several parameters such as extractant types and concentration, diluents, and metal ions types and concentration. Several organo-phosphorous compound such as cyanex272, D2EHPA, cyanex 301 and 302 have been employed for the extraction of silver from various systems. Other extractants such as chelating like dithizone and tetra methylthiuram disulfide, solvating extractant such as MIBK and cyanex 471X and several types of calixarene and crown ether were also used for the extraction of silver. Sulphur substituted phosphinic acid like cyanex 302 and cyanex 301 are employed as extractants for the extraction studies of transition metals.

Cobalt exists in two oxidation states: cobalt (II) or cobaltous ion, Co$^{2+}$ and cobalt (III) or cobaltic ion, Co$^{3+}$. Cobalt (II) forms the coordination complexes which are exhibiting considerable activities towards pathogenic bacteria. Cobalt is not considered to be as toxic as most of the heavy metals, although insufficient or excessive intake may lead to deficiency or toxicity that results in flushing, vasodilatation and cardiomyopathy in humans and animals.

Many organic reagents having sulphur as coordinating atom such as dithizone, N,N-ethylene-bis(o-mercaptobenamide) and thioumrithr trifluoro acetone have been used in the determination of cobalt(II) in real samples. The extraction and separation of cobalt is
of great relevance and interest with the increasing demand for this metal and its compounds. Solvent extraction appears to the economic performance for a replacement of the conventional separation methods. For the extractive separation of cobalt, copper and nickel from aqueous solutions, either oxime or organo phosphorous based extractants is often employed\(^3\). Among the most effective extractants are 2-

(4- Carboxy methylphenyl) azo ]-4,5-

diphenyl imidazole (4 - CMePADPI) as a sensitive and selective ligand for the extraction of cobalt(II) ions from aqueous solutions has been successfully carried out\(^4\). Many other organic ligands have been used in solvent extraction of Co\(^{II}\) from both aqueous and real samples and these include 4-(2-pyrydylazo)resorcinol (PAR), 1,4-diphenyl-3-(phenylamino)-1H-1,2,4-triazole (Nitron, Nt), water, and chloroform\(^5\); bis(2-diethylhexyl)phosphoric acid (DEHPA) and 2-thienyltrifluoroacetone (HTTA) \(^6\); 1-phenyl-3-methyl-4-(p nitrobenzoyl)pyrazolone (HPMNP)\(^7\) and 2-[(4-Chloro -2-methoxy phenyl azo ]-4,5-
diphenyl imidazole (4-CMePADPI)\(^8\). Bis (2-ethylhexyl) phosphoric acid (DEHPA) and 2-thienyltrifluoroacetone (HTTA) are efficient extractants for Cd, Co and Ni ions and the selectivity and efficiency of the process are profoundly affected by the aqueous phase pH and the type of organic diluent\(^9\). The objectives of this work were to synthesize an organic ligand namely, 1,5-dimethyl-2- phenyl]-4-

[(E)-(2,3,4-trihydroxyphenyl) diazenyl]-1,2-dihydro-3H-pyrazole-3-one (H\(_3L\)) and use the synthesized ligand to extract Co(II) from aqueous solution at varying extraction conditions.

### Materials and Methods

#### Equipment

The pH values of buffer solutions and sample solutions were checked with universal pH indicator paper and Jenway 3510 pH meter. Ground – glass-stoppered bottles of 20 cm\(^3\) capacity were used for all equilibration. A multifix mechanical shaker type M80 with left-right directional revolution speed control and timer units was used for all the shakings. Each phase separation was effected by using 60 ml syringe. Melting point was determined with Fisher-Johns melting point apparatus. VIS Spectrophotometer S23A Medifield equipment and scientific England, 721 VIS spectrophotometer and UV visible spec Jenway 6305 spectrophotometer. The infrared spectra were measured with Shimadzu spectrophotometer. The conductivity of the ligand and the complexes were measured with LF – 90; W TW (model)-conductivity meter.

#### Preparation of metal stock solution

Standard solution of cobalt (II) containing 30 µg/ml was prepared by dissolving 0.123 g of cobalt (II)chloride hexahydrate CoCl\(_2\) \(6\)H\(_2\)O, in 1 litre of distilled water.

#### Preparation of pH solutions

Clark and Lubb’s procedure\(^10\) was used to prepare standard solution covering pH range 1-13 with standard of the following acids/ salts systems; hydrochloric acid / potassium chloride, hydrochloric acid / potassium hydrogen phthalate, potassium hydrogen phthalate/ sodium hydroxide, and boric acid/ sodium hydroxide. They were standardized using a universal indicator paper and Jenway 3510 pH meter.

#### Preparation of acids, salting out agents and masking agents

Solutions of 2.0 M HCl : 2.0 M H\(_2\)SO\(_4\); 2.0 M HNO\(_3\) and 2.0 M HClO\(_4\) were each prepared in a 100 cm\(^3\) standard flask according to classical method. Also, 2.0 M NaCl; 2.0 M Na\(_2\)SO\(_4\); 2.0 M KNO\(_3\); 2.0 M KCN; 2.0 M EDTA and 2.0 M Potassium hydrogen phthalate solutions were similarly prepared for salting out and masking interfering metallic ions.

#### Spectrophotometric reagents

2.0 M Ammonium thiocyanate was prepared by weighing out exactly 9.72 g of potassium thiocyanate and dissolving in 50 % (w/v) of acetone and made up to the mark in a 100 cm\(^3\) standard flask.\(^\text{11}\) Sythesis of 1, 5-dimethyl-2-phenyl-[4(E)-(2,3,4-

trihydroxy phenyl)diazenyl]-1,2- dihydro 3H-

pyrazole-3-one [H\(_3L\)]. The azo ligand was synthesized following the Heinosuke Yasuda method\(^\text{12}\) and recently employed by Agbo and Ukoha\(^\text{13}\). It was done by dissolving 4-

aminoantipyrine in dilute hydrochloric acid and diaotizong with sodium nitrite solution below 5 \(^\circ\)C with hand stirring. The resulting 4-aminoantipyrine was poured into a solution of 1,2,3-

trihydroxybenzene and sodium acetate using mechanical stirring at room temperature. The product was left overnight, filtered and washed with methanol. The compound was recrystallized and stored in a desiccators over CaCl\(_2\). A mass of 8.0\(\times\)10\(^{-3}\) g of the ligand (H\(_3L\)) was weighed and dissolved in chloroform and made up to mark in a standard flask for cobalt(II) extraction.

#### Stoichiometric Studies

Stoichiometric studies were carried out using Job’s continuous variation method of analysis\(^\text{14}\). This was done by preparing 0.001 M of the synthesized ligand and the metal salt. For each reaction performed, a total of 11 different mixtures were made .This involved varying the volumes of the metal solution and ligand to make a volume of 1.0 ml. Absolute ethanol (4 ml) was added into each mixture. These mixtures were corked, shaken and then allowed to stand for 20 min. Their absorbances obtained were plotted against the mole ratio of each mixture and the...
complex’s stoichiometry was determined from the curve.

**Extraction Procedures**

Extraction procedure in literature was adopted\(^{23}\). Solutions of both organic and aqueous phases were allowed to equilibrate at room temperature 27±1°C before mixing. All extractions were carried out at the temperature stated. The time taken by the metal complex to transfer from aqueous phase into organic phase called the equilibration time of metal complex was investigated in buffer solution. 30 µg/ml of Co (II) solution (1 ml) each was pipette into different extraction bottles, and 1.5 of buffer (pH 6.0) added and made up to 5 ml with distilled water. Equal volume (5 ml) of \(8.0 \times 10^{-3}\ %\) solution of \(H_3L\) in chloroform was added into each bottle. The mechanical shaker was set at a high constant speed such that increase in agitation speed did not change the extraction rate. The bottles were shaken and one bottle removed after each of desired time interval, 5,10,20,30,40,50,60,70,80,90 minutes. The two phases were centrifuged and separated. The amount extracted in the organic and unextracted in the aqueous phases was determined spectrophotometrically after reaction with 1.0 M ammonium thiocyanate /acetone solution.

**Extraction from Buffer Solution**

1 ml of 30 µg of the Co\(^{2+}\) standard solution was pipetted into different extraction bottles to cover a pH range 1-13. 1.5 ml of the buffer solution of known pH was added into each bottle. The solutions were adjusted to the required pH using either dilute hydrochloric acid or ammonium solution and finally made up to 5.0 ml with the corresponding buffer solution. 5.0 ml of \(8.0 \times 10^{-3}\ %\) \(H_3L\) in chloroform was added to each of the extraction bottles. The phases were equilibrated, centrifuged and separated. The amount of metal ion extracted into the organic phase and that unextracted in the aqueous phase was determined using UV-VIS Spectrophotometer.

**Extraction in acid media**

1 ml of 30 µg/ml solution of metal ion under study was pipetted into different extraction bottles and the appropriate volume of the acid (\(H_2SO_4\), HCl, \(HNO_3\) or \(HClO_4\)) was added such that on final dilution to 5 ml with distilled water the concentration range 0.001-2.0 M was covered. Equal volume of \(8.0 \times 10^{-3}\ %\) of \(H_3L\) in chloroform was added and the mixture equilibrated. The amount of metal extracted and unextracted was determined using UV-VIS Spectrophotometer.

**Extraction in salting out agents**

1 ml of 10 µg/ml or 30 µg/ml solution of metal ion under study was pipetted into different extraction bottles. Appropriate volume of salting out agent (\(KNO_3, Na_2SO_4, KClO_4\) or \(NaCl\)) was added to cover the concentration range 0.001-1.0 M in \(HNO_3, H_2SO_4, HClO_4\) or HCl respectively at the acid concentrations that gave partial extraction all in 5 ml final solution. 5 ml of \(8.0 \times 10^{-3}\ %\) \(H_3L\) in chloroform was added into each bottle and the phases equilibrated for the appropriate time determined for each metal. The phases were centrifuged and separated, and the amount of metal ion extracted and unextracted in both phases were determined using UV-VIS Spectrophotometer.

**Extraction in masking agents**

1 ml of 10 µg/ml or 30 µg/ml solution of metal ion under study was pipetted into different extraction bottles. Appropriate volume of masking agent (cyanide, oxalate, EDTA, tetratate, potassium hydrogen phthalate) solution was added separately to the extraction mixtures. The concentration range of the masking agents was maintained between 0.001 – 1.0 M at the concentration of acid where quantitative extraction was obtained. The mixture was made up to 5 ml final solution. 5 ml of \(8.0 \times 10^{-3}\ %\) \(H_3L\) in chloroform was added into each bottle and the phases equilibrated for the appropriate time determined for each metal. The phases were centrifuged and separated, and the amount of metal ion extracted and unextracted in both phases were analysed using UV-VIS Spectrophotometer.

**Distribution Ratio (D)**

The distribution ratio of the metal was evaluated as the ratio of the concentration of the metal ion in the organic phase to that in the aqueous phase as shown in the equation:

\[
D = \frac{\text{Concentration of metal in organic phase}}{\text{Concentration of metal in aqueous phase}}
\]

**Results and Discussions**

**Authentication of \(H_3L\) and its Co(II) Complex.**

Physical characterisations, molar conductivities data, spectroscopic data and stoichiometric ratio study data obtained for the ligand and the complex agree completely with information earlier reported\(^{22}\). The structures of the ligand and the complex are\(^{24}\).

Figure 1: Structure for \(H_3L\)
Table 4: Amount of Co (II) extracted into the organic phase at various time intervals

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Co(II) in organic phase (µg/ml)</th>
<th>Co(II) in aqueous phase (µg/ml)</th>
<th>Percentage extracted (%E)</th>
<th>Distribution ratio (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>24.75</td>
<td>5.25</td>
<td>82.50</td>
<td>4.71</td>
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<tr>
<td>10</td>
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</table>

**Effect of equilibration time on solvent extraction of Co by H₃L**
The equilibration time of Co (II) ions was carried out with 8.0 x 10⁻³ % H₃L in chloroform. The percentage extracted at different time intervals are shown in Table 4.

During the extraction of Co (II), optimum extraction was obtained at an equilibration time of 10 min. Thus subsequent extractions were carried out at 10 min.

**Effect of pH on the extraction of Co (II).**
The effect of pH on the extraction of Co (II), in buffer solution was carried out with 8.0 x 10⁻³ % H₃L in chloroform. A maximum extraction of 91.66 % is reached between 9 and 13 as shown in Figure 4. Low extraction at pH 1 to 8 could be due to the competition between the protons and Co(II) ion for ligand coordination sites.

**Effect of acidity on extraction of Co (II)**
The effect of acidity on the extraction of Co(II) at various acid concentration is displayed in Fig 5. The result shows that acid concentration 10⁻³-10⁻² also supports the formation of extractable ionic complex.

**Figure 4: Profile for Co (II) extraction in buffer media.**

In acid concentration of 10⁻³ H₂SO₄ up to 81.2 % of Co (II) was extracted. It also shows that percentage extracted decrease with increase in acidity. Lower extraction was observed in HCl than in any other acid. Increased extraction in acid concentration 10⁻³ may likely be due to the replacement of attached proton on
the ligand by Co(II) for ligand coordination sites. Low extraction in HCl could be as a result of formation of non-extractable complex [CoCl₄]²⁻ which could diminish the extraction of the metal at high chloride concentration.

**Figure 5: Profile for extraction of Co(II) in various acid media.**

**Effect of Salting–Out Agent on the Extraction**

Extraction of Co(II) with 8.0×10⁻³ was studied at different concentration of salting out agents (NaCl, Na₂SO₄, NaClO₄ and KNO₃) in acid medium where there is only partial extraction of the metal. Fig 6 shows that extraction was enhanced from 29.99 to 87.5 % in 2.0 M HClO₄ on addition of 0.001 M KClO₄. At 2.0 M H₂SO₄, extraction was enhanced from 39.17 to 91.67 % with the addition of 0.001 M of Na₂SO₄. Increase in extraction on addition of both 0.001 M KClO₄ and 0.001 M Na₂SO₄ was as a result of increase in dielectric constant of the aqueous phase which makes the complex less ionic, hence more soluble in the organic phase. At 2.0 M HCl, the amount extracted increased from 27 to 87.5 % at 0.5 M NaCl, the amount extracted increased with increase in concentration (10⁻³-0.5 M). This is a result of formation of extractable complex which is soluble in the organic phase. At 1.0 M, a slight decrease in the amount extracted was observed. Extraction was enhanced from 23.75% to 66.7% in 0.001 M KNO₃. This is likely due to formation of extractable complexes soluble in the organic phase. From the above analysis, it was observed that 0.001 M KClO₄, Na₂SO₄ and 0.5 M NaCl are good salting out agents for the extraction of Co(II).

**Figure 6 : %E against concentration of various salting out agents for the extraction of Co(II) with H₃L/CHCl₃**

**Effects of masking agents on extraction of Co (II)**

The effect of masking agents on the degree of extraction was also investigated at acid concentration of quantitative extraction of Co (II). The effect of masking agents on the extraction of Co (II). KCN and EDTA greatly decreased the extraction of Co (II). At 0.1 M EDTA masked up to 77.03 % of the Co (II) while at 1.0 M the masking effect reduced to 56.2 %. At 0.1 - 0.5 M KCN masked up to 72.87 % of Co(II) where as at 1.0 M the masking effect reduced to 62.45 %. Oxalate masked Co (II) up to 64.53 % at 0.1 M concentration. At 0.001 M potassium hydrogen phthalate masked up to 35.4 % while at 1.0 M concentration only 6.2 % of Co (II) ion was masked.

Sodium potassium tartrate at 0.001 M masked up to 10.4 % of Co (II). However at 1.0 M concentration it had no significant effect on the extraction of Co (II) ion. High masking of Co(II) in the presence of EDTA, KCN, ammonium oxalate is likely to be as a result of formation of non-extractable complex formed at the aqueous phase. The partial extraction observed in potassium hydrogen phthalate may be as a result of formation of unstable complex which is slightly soluble in the organic phase. The little or no masking effect observed in NaK-tartrate in the extraction of Co(II) may be due to formation of unstable complex which is soluble in the organic phase.
In summary, extraction of Co(II) up to 81.2% was observed in 10^-3 M H_2SO_4 medium. The result showed that the amount extracted decreased with increase in acid concentration. Na_2SO_4 and KClO_4 proved to be good salting out agents for the extraction of Co(II). The ligand is a good extractant for Cobalt (II) in the studied conditions.

References