

## Extraction of $\text{Cu}^{2+}$ , $\text{Co}^{2+}$ and $\text{Ni}^{2+}$ ions from aqueous solutions of bromide ion using 1- phenyl -3- methyl -4- trichloro acetyl pyrazolone - 5 in benzene and hexane.

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**Abstract:** Extraction of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions from aqueous solutions of bromide ion using 1- phenyl -3- methyl -4- trichloro acetyl pyrazolone - 5 (HTcP) in benzene and hexane organic medium have been studied. From the results, extraction of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions were masked by anionic complexes of the bromide ions throughout the pH range of 0 – 7 studied. However,  $\text{Cu}^{2+}$  ions were quantitatively extracted from aqueous solutions of bromide ions, thus presenting an analytical technique for the efficient separation of  $\text{Cu}^{2+}$  ions from  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions. Increase in bromide ion concentration from 0.05 to 0.3M had a salting out effect on the extraction of  $\text{Cu}^{2+}$  ions from 97.44% to 98.79% in benzene/HTcP medium and 97.13% to 98.33% in hexane/HTcP. On application of statistical treatment using slope analysis, the values of  $\text{pH}_{1/2}$ ,  $\log K_{\text{ex}}$  and  $\log K_{\text{d}}$  have been calculated and presented. Hence the complex formed is  $\text{Cu}(\text{TcP})_2$ . Generally, extraction of  $\text{Cu}^{2+}$  ions was found to be more efficient in hexane/HTcP at relatively lower pH value in comparison to extraction into benzene/HTcP, while optimal percentage yield was slightly higher in benzene/HTcP than hexane/HTcP solution. This has been attributed to lower dielectric constants of hexane (2.02) and lower dipole moment in comparison to that of benzene (2.28). Finally, molecular modeling shows that the stable structure of the ligand derivative (HTcP) was quite different in orientation from the parent ligand (1- phenyl -3- methyl -4- acyl pyrazolone – 5- HPMAP) and has been attributed to the bulky nature of the trichloro unit. [Chukwu U. John, Uzoukwu B. Augustus. **Extraction of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions from aqueous solutions of bromide ion using 1- phenyl -3- methyl -4- trichloro acetyl pyrazolone - 5 in benzene and hexane.** *Rep Opinion* 2014;6(9):95-101]. (ISSN: 1553-9873). <http://www.sciencepub.net/report>. 15

**Keywords:** buffer solutions; Liquid-liquid extraction; slope analysis

### 1. Introduction

In continuation of our study on the extraction behavior of the ligand 1 -phenyl - 3 - methyl- 4 – trichloro acetyl pyrazolone -5 (HTcP) in the extraction of some divalent metals from various halide ion concentrations into benzene and hexane solutions (Uzoukwu and Mbonu, 2005; Chukwu and Uzoukwu, 2008; Chukwu and Uzoukwu, 2010), the extraction of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions from aqueous bromide ion solutions using the ligand (HTcP) into benzene and hexane medium was studied. The role of liquid- liquid extraction and separation techniques cannot be over emphasized especially in hydrometallurgy industries (Atanassova, 2006<sup>b</sup> Ogwuegbu and Oforka, 1994), in the pharmaceuticals (Cyr, 2009; Malick, et al, 2009), soil remediation (Aurora, et al, 2005) and separation of transition metals [Atanassova and Dukov, 2006<sup>a</sup>; Atanassova and Dukov, 2004; Bukowsky, et al, 1992) to mention a few.

Various studies have been carried out on liquid – liquid extraction and separation techniques using 1 -phenyl - 3 - methyl- 4 - acyl pyrazolone -5 by many workers (Okafor and Uzoukwu, 1990; Okafor, et al, 1993; Uzoukwu and Adiukwu, 1996<sup>b</sup>; Uzoukwu and Nwachukwu, 1994). Introduction of various synergists have further improved the

efficiency of these ligands in solvent extraction studies (Umetani et al 1990; Atanassova and Dukov, 2006<sup>b</sup>; Bond et al, 1999). More so, the trichloro acetyl derivative (HTcP) has proven to be a good metal extractant, due to its low pKa value ( $3.02 \pm 0.05$ ) (Uzoukwu, 1991<sup>a</sup>). In addition, it is a  $\beta$ -diketone and can exhibit four (4) different tautomers (Okafor et al, 1993). The effect of chloride ion in a buffer medium on the extraction of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  using the trichloro acetyl derivative (Uzoukwu and Mbonu, 2005) and extraction of  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  using the same ligand HTcP have equally been studied (Chukwu and Uzoukwu, 2008; Chukwu and Uzoukwu, 2010), and an efficient method for the separation of these metals developed (Uzoukwu and Mbonu, 2005).

Hence the present study is aimed at investigating the extraction behavior of this ligand (HTcP) from aqueous solutions of bromide ion containing  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions.

### 2. Material and Methods

Reagents of analytical grade (Aldrich or BDH) were used. They include HTcP,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NiSO}_4(\text{NH}_4)_2 \cdot 7\text{H}_2\text{O}$ , NaBr, HCl, Benzene, Hexane and 95% ethanol. Deionized water was used throughout the experiment.

## 2.1 Procedure

The ligand was synthesized by methods described elsewhere (Jensen, 1959). The ligand was twice recrystallised from aqueous ethanol after synthesis. Thereafter, the purity was further established by UV, IR, NMR spectral methods and elemental analysis for C, H, and N. The elemental analysis of the ligand was carried out using a Euro EA Elemental Analyzer at Fortungszentrum Rossenderf Dresden, Germany. Stock solutions of  $10^{-2}$  M of HTcP were prepared by dissolving an appropriate mass (0.3195g) of the ligand in 100ml of benzene and hexane each. Stock solution of the metal ion ( $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$ ) each, was prepared by dissolving the appropriate mass of salt for the metal in 2ml of 0.01 M HCl in a 100ml volumetric flask and making up to mark using deionized water. Buffer solutions containing 0.05M, 0.1M and 0.3M  $\text{Br}^-$  ions, were prepared and the pH determined using a Consort C531 pH/conductivity meter

The aqueous phase was made up of 2ml aliquot of a buffer solution containing the metal ion and the desired bromide ion solution. An equal volume (2ml) of a benzene or hexane solution containing 0.01M of HTcP made up the organic phase. This mixture was shaken mechanically for 45 minutes at room temperature. A shaking time of 45 minutes was found to be enough for equilibration. The phases were allowed to settle and then separated for analysis of the metal ion in the aqueous raffinate. Metal ion concentration in the aqueous raffinate was determined using a Bulk Scientific Atomic Absorption Spectrophotometer (200A model).

The concentration of metal ion extracted into the organic phase was determined by difference. Distribution ratio,  $D$ , was calculated as the ratio of metal ion concentration in organic phase ( $C_o$ ) to that in the aqueous phase ( $C$ ) thus,  $D = C_o/C$  (Uzoukwu, 2009).

## 3. Results and Discussion

The experimental values obtained for elemental analysis of Carbon (C), Hydrogen (H) and Nitrogen (N) were very comparable to calculated values as shown in table 1.0. The electronic spectra of the ligand HTcP exhibited two broad absorption bands  $\lambda_1$  near 251nm and  $\lambda_2$  near 295nm in the ultraviolet region with molar absorptivities of  $\epsilon_1$  0.27 and  $\epsilon_2$  1.31 respectively. Furthermore, the statistical treatment applied to this work has earlier been reported (Chukwu and Uzoukwu, 2010); Uzoukwu et al, 1998).

Table 1.0 Data for Elemental Analysis of HTcP

Element	Calculated Values (%)	Experimental Values (%)
Carbon (C)	45.10	45.39
Hydrogen (H)	2.84	2.82
Nitrogen (N)	8.77	8.74

## 3.1 Extraction of $\text{Cu}^{2+}$ , $\text{Co}^{2+}$ and $\text{Ni}^{2+}$ From Buffer Solutions Containing $\text{Br}^-$ at different pH Values

Extraction of  $\text{Cu}^{2+}$  ions from aqueous buffer solutions containing various bromide ions (0.05M, 0.1M and 0.3M) into 0.01M HTcP in benzene and hexane showed that quantitative extraction above 90% yield occurred between pH 1.5 to 4.0. This was in contrast to extraction of both  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  which were not extracted throughout the pH range of study (0-7). This has been attributed to the formation of very stable bromo nickel and bromo cobalt complexes which cannot be extracted in this medium (Lee, 1996). Similar results have been reported in the extraction of  $\text{Ni}^{2+}$  ions (Uzoukwu and Mbonu, 2005) and  $\text{Co}^{2+}$  ions (Chukwu and Uzoukwu, 2008) from solutions of aqueous chloride ions using 0.01M HTcP in benzene and hexane. Thus, a separation technique for  $\text{Cu}^{2+}$  from  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  ions has been proposed. The extraction plots of  $\text{Cu}^{2+}$  from aqueous  $\text{Br}^-$  medium into 0.01M HTcP/benzene and HTcP/hexane is presented in figs. 1 and 2 respectively.

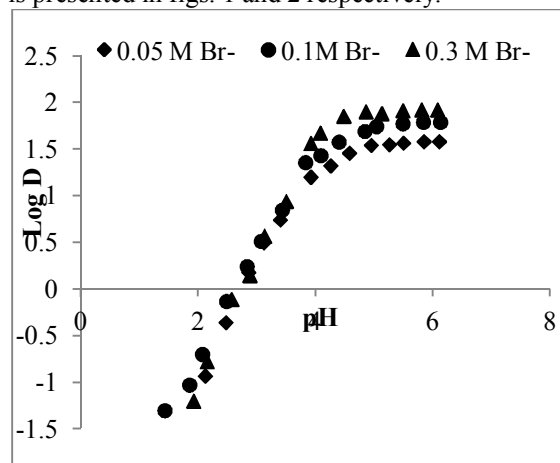


Figure 1: Extraction of copper (II) ion from aqueous solutions of 0.05M  $\text{Br}^-$ , 0.1M  $\text{Br}^-$ , and 0.3M  $\text{Br}^-$  using HTcP in benzene organic medium

From fig. 1, optimal percentage extraction yield of 97.44%, 98.39% and 98.78% were obtained for 0.05M, 0.1M and 0.3M bromide ions with  $\log K_d$  values of 1.58, 1.78 and 1.91 respectively. This shows that, increase in bromide ion concentration gives a corresponding increase in optimal percentage extraction. Therefore, solutions of bromide ions have a salting out effect on the extraction of  $\text{Cu}^{2+}$  using

0.01M HTcP in benzene medium. Similar results have been reported by previous workers in the extraction of  $\text{Cu}^{2+}$  from solutions of chloride ions (Uzoukwu and Mbonu, 2005). A slope of 2 was obtained in all cases which is an indication that 2 protons were displaced during the extraction process. Such displacement of protons during extraction by metal ions with chelating agents has been reported (Chukwu and Uzoukwu, 2010; Atanassova and Dukov, 2006<sup>b</sup>; Pavithran and Reddy, 2003). The  $\text{pH}_{1/2}$  was found to be approximately  $2.70 \pm 0.02$  irrespective of the bromide ion concentration. Log  $K_{\text{ex}}$  on the other hand increased from 0.05M with value of  $-1.74 \pm 0.02$  to 0.1M with value of  $-1.65 \pm 0.02$  and 0.3M with value of  $-1.60 \pm 0.02$ . This shows that solutions of 0.3M bromide ions is a relatively better medium for the extraction of  $\text{Cu}^{2+}$  ions into 0.01M HTcP/benzene organic media. Table 2.0 summarizes the extraction data of  $\text{Cu}^{2+}$  ions for 0.05M, 0.1M and 0.3M  $\text{Br}^-$  into 0.01M HTcP/benzene.

Table 2.0 Extraction data of copper (II) ions for 0.05M  $\text{Br}^-$ , 0.1M  $\text{Br}^-$  and 0.3M  $\text{Br}^-$  in benzene solutions containing 0.01M HTcP.

	0.05M $\text{Br}^-$	0.1M $\text{Br}^-$	0.3M $\text{Br}^-$
Slope	$2.00 \pm 0.02$	$2.00 \pm 0.02$	$2.00 \pm 0.02$
$\text{pH}_{1/2}$	$2.70 \pm 0.02$	$2.70 \pm 0.02$	$2.70 \pm 0.02$
%E	$97.44 \pm 0.10$	$98.39 \pm 0.10$	$98.78 \pm 0.10$
Log $K_d$	$1.58 \pm 0.05$	$1.78 \pm 0.05$	$1.91 \pm 0.05$
Log $K_{\text{ex}}$	$-1.74 \pm 0.05$	$-1.63 \pm 0.05$	$-1.61 \pm 0.05$

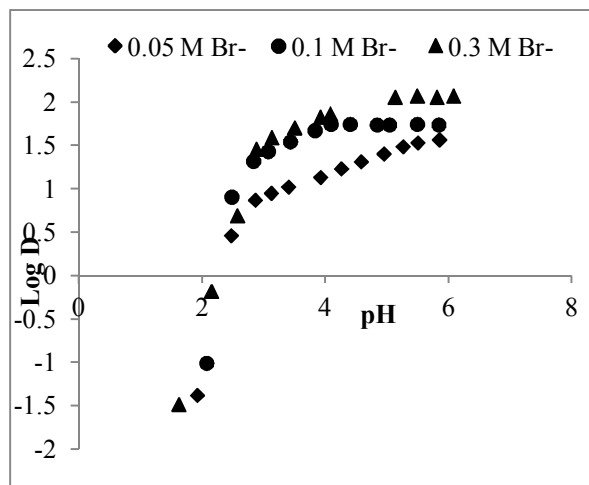


Figure 2: Extraction of copper (II) ion from aqueous solutions of 0.05M  $\text{Br}^-$ , 0.1M  $\text{Br}^-$ , and 0.3M  $\text{Br}^-$  using HTcP in hexane organic medium

Extraction plots of  $\text{Cu}^{2+}$  from buffer solutions containing various bromide ions into 0.01M HTcP in hexane medium are shown in fig. 2. From the plots, optimal percentage extraction of 97.13%

for 0.05M, 98.09% for 0.1M and 98.33% for 0.3M were obtained while log  $K_d$  values obtained for the three different bromide ion solutions were  $1.53 \pm 0.05$ ,  $1.73 \pm 0.05$  and  $1.90 \pm 0.05$  for 0.05M, 0.1M and 0.3M bromide ions respectively. Again, showing that increase in bromide ion concentration gives a corresponding increase in optimal percentage extraction. Thus, solutions of bromide ions have a salting out effect on the extraction of  $\text{Cu}^{2+}$  ions using 0.01M HTcP in hexane medium same with solutions of 0.01M HTcP in benzene. A look at  $\text{pH}_{1/2}$  values (table 3.0) shows that extraction into hexane solutions of 0.01M HTcP was more efficient at relatively lower pH value ( $2.30 \pm 0.02$ ) in comparison to extraction into benzene solutions of same, while optimal percentage yield was relatively higher with benzene solutions rather than with hexane solutions of 0.01M HTcP. This has been attributed to lower dielectric constants of hexane (2.02) and lower dipole moment in comparison to benzene (2.28) (Lee, 1996; Cotton and Wilkinson, 1985). This is similar to previous work by Uzoukwu and Mbonu (2005) on the effects of  $\text{Cl}^-$  ion concentration on the extraction of  $\text{Cu}^{2+}$  ion using HTcP in benzene and hexane. Table 3.0 summarizes the extraction data of  $\text{Cu}^{2+}$  for 0.05M, 0.1M and 0.3M  $\text{Br}^-$  into 0.01M HTcP/hexane.

Table 3.0 Extraction data of copper (II) ions for 0.05M  $\text{Br}^-$ , 0.1M  $\text{Br}^-$  and 0.3M  $\text{Br}^-$  in hexane solutions containing 0.01M HTcP.

	0.05M $\text{Br}^-$	0.1M $\text{Br}^-$	0.3M $\text{Br}^-$
Slope	$2.00 \pm 0.02$	$2.00 \pm 0.02$	$2.00 \pm 0.02$
$\text{pH}_{1/2}$	$2.30 \pm 0.02$	$2.30 \pm 0.02$	$2.30 \pm 0.02$
%E	$97.13 \pm 0.10$	$98.09 \pm 0.10$	$98.33 \pm 0.10$
Log $K_d$	$1.53 \pm 0.05$	$1.73 \pm 0.05$	$2.05 \pm 0.05$
Log $K_{\text{ex}}$	$-0.85 \pm 0.05$	$-0.71 \pm 0.05$	$-0.67 \pm 0.05$

### 3.2 Slope Analysis of the Extraction of $\text{Cu}^{2+}$

Statistical treatment of data applied to this work has earlier been reported (Chukwu and Uzoukwu, 2010; Uzoukwu et al, 1998). Plots of the variation of Log D with Log [HTcP] for the extraction of  $\text{Cu}^{2+}$  into benzene solutions from 0.3M  $\text{Br}^-$  at three different pH values is presented in fig 3. In each curve, a slope of 2 was obtained suggesting that the interaction between  $\text{Cu}^{2+}$  and the ligand involved 2 moles of the ligand. Previous works (Ogwuegbu and Oforka, 1994; Pavithran and Reddy, 2003) have shown that 2 moles of protons were released during similar interaction.

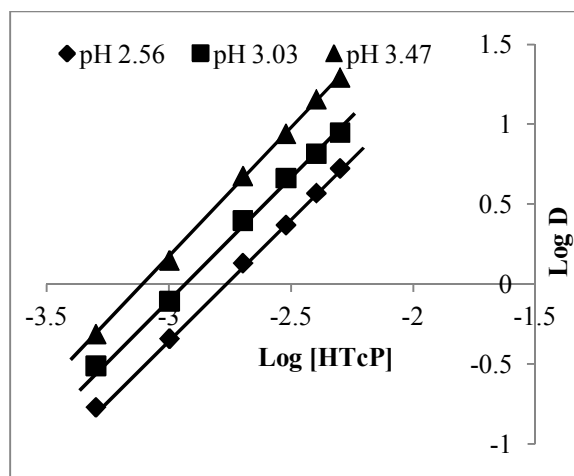


Figure 3: Extraction of copper (II) ions at constant pH and 0.3M Br<sup>-</sup> into varying ligand conc. [HTcP] in Benzene medium.

The degree of extraction as a function of Cu<sup>2+</sup> ion concentration is presented in fig. 4 at constant pH values of 2.56, 3.03 and 3.47, each containing 0.03M Br<sup>-</sup> in 0.01M HTcP/benzene solution. From the plots in fig 4, a slope of zero (0) was obtained; on applying statistical treatment (Chukwu and Uzoukwu, 2010; Uzoukwu et al, 1998), the interaction involved 1 mole of metal (Cu<sup>2+</sup>) ion at each of the pH value studied. Hence the metal ligand ratio was 1:2 and the complex formed under this condition is Cu(TcP)<sub>2</sub>. This result is in agreement with results obtained by previous workers (Uzoukwu and Mbonu, 2005; Chukwu and Uzoukwu, 2008; Chukwu and Uzoukwu, 2010).

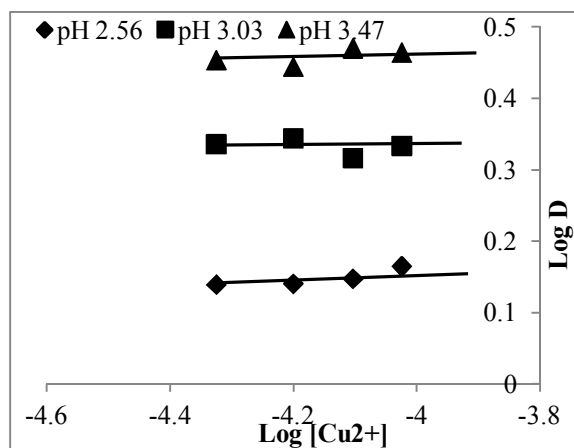
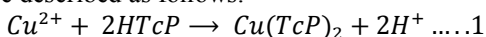


Figure 4: Extraction of copper (II) ions at constant pH and 0.3M Br<sup>-</sup> into varying metal ion conc. [Cu<sup>2+</sup>] in Benzene medium.

Hence, the extraction process for Cu<sup>2+</sup> can be described as follows:



$$D = \frac{[Cu(TcP)_2]_{(o)} [H^+]^2}{[Cu^{2+}] [HTcP]^2} \dots \dots 2$$

$$\log D = \log K_{ex} + \log[Cu^{2+}] + 2 \log[HTcP] + 2pH \dots \dots 3$$

#### 4.0 Molecular Modeling Computation

Molecular modelling computation for the ligand (HTcP) and metal complex formed above were carried out using the HyperChem molecular modelling and mercury software packages. This was to provide an insight into the structural forms of the ligand and the complex formed. Bond lengths and bond angles were further calculated and values compared with published works (Uzoukwu et al, 1996<sup>a</sup>; Uzoukwu et al, 1996<sup>b</sup>; Uzoukwu et al, 2004).

From fig. 5, it was observed that the stable structure of the modelled ligand derivative (HTcP) is quite different from the modelled structure of 1-phenyl-3-methyl-4-acetyl pyrazolone-5 (HPMAP) as reported by Uzoukwu, et al (2004). According to the modelled structure (fig. 5) the position of O-H and C=O appear twisted in comparison to that of (HPMAP). This “twisted” form of the trichloro derivative is quite different from the modelled structure of 1-phenyl-3-methyl-4-acetyl pyrazolone-5 as reported by Uzoukwu, et al (2004) and the butyryl derivative of the ligand. The change in orientation could be attributed to the bulky nature of the trichloro unit which forces the C=O and O-H groups to assume an angle of about 180°. However, the bond angles and bond lengths of the modelled derivative HTcP are very similar to that published by previous workers as tabulated in table 4.0 (Uzoukwu et al, 1996<sup>a</sup>; Uzoukwu et al, 1996<sup>b</sup>; Uzoukwu et al, 2004).

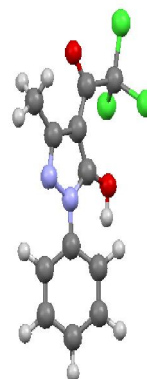
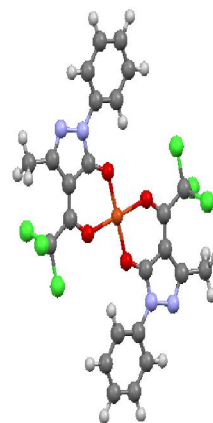


Figure 5: Molecular modelled structure of 1-phenyl-3-methyl-4-trichloroacetyl pyrazolone -5 (HTcP).

Table 4.0: Intra molecular bond lengths (Å) and angles (°) for the synthesized 1-phenyl-3-methyl-4-trichloroacetyl pyrazolone -5 (HTcP) obtained from molecular modelling computation

Bond Type	Bond Length (Å)	Bond Type	Bond Angle (Deg)
O - H	0.974	Cl - C - Cl	108.55
C = O	1.217	C-O-H	109.73
C - O	1.339	C-C = O	124.48
N = N	1.383	C -N - C	127.89
N - C	1.318	N = N - C	120.30
C - Cl	1.805		
C - H	1.087		

Interestingly, fig. 6 shows the modelled structure of the metal ( $\text{Cu}^{2+}$ ) complex with the ligand HTcP. This stable metal complex again changed the orientation of both the C=O and O-H bonds in complexing with the metal. Again, values of their bond lengths and angles have been calculated and presented in table 5.0.

Figure 6: Molecular modelled structure of the complex  $\text{Cu}(\text{TcP})_2$  formed.Table 5.0: Intra molecular bond lengths (Å) and angles (°) for the synthesized complex  $\text{Cu}(\text{TcP})_2$  formed obtained from molecular modelling computation

Bond Type	Bond Length (Å)	Bond Type	Bond Angle (Deg)
Cu-O	1.922	O-Cu-O	91.57, 88.43,
Cu-O	1.882	O-Cu-O	91.57, 88.43
		C-O- Cu	124.47 and 123.36
		C-O- Cu	124.47 and 123.36
		O-C-C	130.75 and 123.37
		O-C-C	130.75 and 123.37

## 5.0 Conclusion

Extraction of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  ions are masked by aqueous solutions of bromide ions as a result of stable bromo Nickel and bromo Cobalt complexes within the pH range of 0 -7 studied.  $\text{Cu}^{2+}$  ions on the other hand are quantitatively extracted from aqueous solutions of bromide ions using 0.01M HTcP in benzene and hexane organic medium. Thus, this presents a potential for the separation of  $\text{Cu}^{2+}$  ions from  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  ions in solution. Increase in bromide ion concentration has a salting out effect on the extraction process. However, extraction into hexane organic medium was more efficient at

relatively lower pH values in comparison to extraction into benzene/HTcP medium, while optimal percentage extraction yield was better in benzene than in hexane. This was attributed to differences in the dielectric constants and dipole moments between benzene and hexane. Using slope analysis of statistical treatment, the complex formed was  $\text{Cu}(\text{TcP})_2$ . Furthermore, molecular modeling of the ligand and the complex was done which showed that the orientation of the stable form of the ligand derivative (HTcP) was slightly different from the parent ligand (HPMAP) and the complex formed  $\text{Cu}(\text{TcP})_2$ .

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**References**

- Atanassova, M. "Synergistic solvent extraction of La(III), Eu(III) and Lu(III) with mixtures of 5,7-dibromo-8-hydroxyquinoline and crown ethers". *Journal of the University of Chemical Technology and Metallurgy*. 2006; 41 (1): 81-84.
- Atanassova, M., Dukov, I. L. "Solvent extraction and separation of lanthanoids with mixtures of chelating extractant and 1-(2-pyridylazo)-2-naphthol". *Separ. Purif. Technol.* 2006a; 49: 101-105.
- Atanassova, M., Dukov, I. L. "Synergistic solvent extraction of trivalent lanthanoids with mixtures of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone and crown ethers". *Acta Chim. Slov.* 2006b; 53: 457-463.
- Atanassova, M., Dukov, I. L. "Synergistic solvent extraction and separation of trivalent lanthanide metals with mixtures of 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one and aliquat 336". *Separ. Purif. Technol.* 2004; 40(2): 171-176.
- Aurora, S., Delerue-Matos C., Fi'uzza A. "Use of solvent extraction to remediate soils contaminated with hydrocarbons". *Journal of Hazardous Materials*. 2005; B124: 224-229.
- Bond, A. H., Chiarizia, R., Huber, V., Dietz, M. L., Herlinger, A. W., Hay, B. P. "Synergistic solvent extraction of alkaline earth cations by mixtures of di-n-octylphosphoric acid and stereoisomers of dicyclohexano-18-crown-6". *Anal. Chem.* 1999; 71: 2757-2765.
- Bukowsky, H., Uhlemann, E., Gloe, K., Muhl P. "Liquid-liquid extraction of alkaline earth and alkali metal ions with acylpyrazolones". *Analytica Chimica Acta*. Elsevier 1992; 257(11): 105-108.
- Chukwu U. J., Uzoukwu, B. A. "Synergistic extraction of  $Zn^{2+}$  from aqueous buffer medium of chloride ions into 1- phenyl -3- methyl -4- Trichloro Acetyl Pyrazolone - 5 in Benzene and Hexane". *Recent Patents on Materials Science*. 2010; 3(2): 146-150.
- Chukwu, U. J., Uzoukwu, B. A. "Effect of chloride ion in a buffer medium on the liquid-liquid extraction of  $Co^{2+}$  using 1-phenyl-3-methyl-4-trichloroacetyl-pyrazolone-5". *Scientia Africana Journal*. 2008; 7(1): 42-50.
- Cotton, F. A., Willikinson, G. "Advanced Inorganic Chemistry, A Comprehensive Text". 3<sup>rd</sup> ed. Mohinder Singh Sejal (New Delhi). 1985.
- Cyr, B. "Methods and Therapeutic Compositions Comprising Plant Extracts for the Treatment of Cancer" Recent patents on Materials Science. 2009. US20090004302.
- Jensen, B. S. "Synthesis of 1-Phenyl-3-Methyl-4-Acyl pyrazolone 5", *Acta Chemica Scandinavia*, (1959). Vol. 13: pp 1668 – 1670.
- Lee J. D. "Concise Inorganic Chemistry". 5<sup>th</sup> ed. Blackwell Science Ltd. USA. 1996.
- Malick, A. P., Crews, V. M., Rosales, J. L., Ferguson, C. S., Bruton, J. H., Beadenkopf, R. J. (2009). "Method of Efficient Extraction of Protein from Cells". Recent patents on Materials Science. US20090123910.
- Ogwuegbu, M. O. C., Oforika, N. C. "Solvent extraction separation studies of iron (III), cobalt (II), nickel (II) and copper (II) from aqueous solution with 1-phenyl-3-methyl-4-(p-nitrobenzoyl)-5-pyrazolone". *Hydrometallurgy*. 1994; 34 (3): 359-367.
- Okafor, E. C., Adiukwu, P. U., Uzoukwu, B. A. "Synthesis and characterization of 4-iso-butyl and 4-iso-valeroyl derivatives of 1-phenyl-3-methyl pyrazolone-5 and their U(VI), Th(IV), La(III), Fe(III), Pb(II) and Ca(II) complexes". *Synth. React. Inorg Met – Org Chem*. 1993; 23(1): 97-111.
- Okafor, E. C., Uzoukwu, B. A. "Extraction of Fe(III) and U(IV) with 1 - phenyl -3- methyl -4- acyl- pyrazolones-5 from aqueous solutions of different acids and complexing agents. Separation of Fe(III) from U(IV)". *Radiochimica Acta*. 1990; 51: 167-172.
- Pavithran, R., Reddy, M. L. P. "Enhanced extraction and separation of trivalent lanthanoids with 3-phenyl-4-(4-fluorobenzoyl)-5-isoxazolone and dicyclohexano-18-crown-6". *Radiochimica Acta*. 2003; 91(3): 163-168.
- Umetani, S., Kihara, S., Matsui, M. "Adduct formation properties of some polydentate phosphine oxides in the synergistic extraction of metals with 4-acyl-5 pyrazolone derivatives". *Solvent Extraction*. 1990; 1992: 309-314.
- Uzoukwu, B. A. "Physiochemical studies of 4-trifluoroacetyl and 4-trichloroacetyl derivatives of 3-methyl-1-phenylpyrazol-5-one and their

- U(VI), Fe(III) and Ca(II) complexes". Indian journal of chemistry. 1991a; 30(A): 372-374.
21. Uzoukwu, B. A. "Basic Analytical Chemistry". Millennium edition. Paragraphics, Port Harcourt. 2009.
  22. Uzoukwu, B. A., Adiukwu, P. U. "Spectroscopic studies of Th(IV), La(III) and Pb(II) complexes of 4-trifluoroacetyl and 4-trichloroacetyl derivatives of 3-methyl-1-phenylpyrazol-5-one". J. Natn. Sci. coun. Sri Lanka. 1996b; 24(3): 221-225.
  23. Uzoukwu, B. A., Adiukwu, P. U., Al-Juaid, S. S., Hitchcock, P. B., David Smith, J. "Pyrazolonato complexes of lead, crystal structures of bis (1-phenyl-3-methyl-4-acetylpyrazolonato) lead (II) and bis (1-phenyl-3-methyl-4-butanoylpyrazolonato) lead (II)". Inorganic Chimica Acta. 1996a; 250: 173-176.
  24. Uzoukwu, B. A., Adiukwu, P. U., Al-Juaid, S. S., Hitchcock, P. B., David Smith, J. "The synthesis and crystal structures of 1-phenyl-3-methyl-4-butanoylpyrazol-5-one and of two pyrazolonato complexes of iron". Polyhedron. 1996b;12 (22); 2719-2724.
  25. Uzoukwu, B. A., Gloe, K., Duddeck, H. "Extraction of Uranium(VI) and Vanadium(V) with 4-Adipyl and 4-Sebacyl derivatives of bis(1-phenyl-3-methyl-pyrazolone-5) and effect of decanol on the distribution behaviour of these metal ions". Solvent Extr. Ion Exch. 1998; 16; 751-774.
  26. Uzoukwu, B. A., Gloe, K., Menzel, M., Wawrzyniak, K. "Syntheses and <sup>119</sup>Sn Mossbauer spectral characterization of tin(IV) complexes of 4-acyl-1-phenyl-3-methyl pyrazolones-5 and molecular modeling of 4-acetyl-1-phenyl-3-methylpyrazolone-5". Indian journal of chemistry. 2004; 43(A); 701-705.
  27. Uzoukwu, B. A., Mbonu, J. I. "Effect of chloride ion in a buffer medium on the liquid-liquid extraction of Cu(II) and Ni(II) using 1-phenyl-3-methyl-4-trichloroacetyl-pyrazolone-5". Solvent Ext. and Ion Exch. 2005; 23(6); 759 - 771.
  28. Uzoukwu, B. A., Nwachukwu, C. K. "Extraction of mineral acid solutions using benzene solutions of 1-phenyl-3-methyl-4-acyl-pyrazolone-5". Indian Journal of Chemistry. 1994; 33(A); 274-276.

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