Chemistry and Materials Research
ISSN 2224- 3224 (Print) ISSN 2225- 0956 (Online)
Vol.6 No.12, 2014

The Substitutional Effects on the Carbonyl and Metal -Oxygen Stretching Frequencies of Some 4-Acyl Functional Derivatives of 1-Phenyl-3-Methyl -4- Acyl Pyrazol -5- ones and Thier Divalent Metal Chelates

Obinna Okpareke[1*] Emmanuel Okafor[1] Pius Ukoha[1] Solomon Okereke[2]
1.Department of Pure and Industrial Chemistry, University of Nigeria Nsukka
2.Department of Industrial Chemistry, Abia State University Uturu.
*Email of the corresponding author : obinna.okpareke@unn.edu.ng.

Abstract
The divalent metal complexes of Mg (II), Co (II), Cu (II) and Zn (II) ions with some 1-phenyl-3-methyl-4-acyl pyrazolone-5 have been synthesized and characterized by physical methods such as elemental analysis , U.V, and I.R spectral analyses. The corroborative evidences from elemental analysis and spectral data show that complexes are neutral dihydrated bischelates conforming to the general formula $ML_2.2\ H_2O$, where $M= Mg^{2+},Co^{2+},Cu^{2+}$ and Zn^{2+} ions and L= anions of the 4-acyl pyrazolone ligand. Infrared spectral assignments(4000 - 400cm-1) were made and interpretation of the spectral data revealed that the stability of C=O bond increased while that of the M=O bond decreased with increase in the number of carbon atoms of the 4-acyl substituent.

Keywords: Stretching frequencies, 4 – acylpyrazolon-5 ,divalent metal chelates.

1. Introduction

Selective solvent extraction of metal ions from aqueous and acidic solutions(Akama et al., 1985, Akama et al., 1986, Coronel et al., 1982, Hasany and Qureshi, 1977, Jyothi and Rao, 1990, Kalagbor et al., 2011, Mirza and NWABUE, 1980, Navratil and Jensen, 1970, Okafor and Uzoukwu, 1990, Ozaki et al., 1989, Uzoukwu et al., 1998a) is a key step in many hydrometallurgical processes. The acyl pyrazolones, an interesting class of β-diketones containing a pyrazole ring fused to a chelate arm, have offered several advantages over other ligands which have been examined as metal extractant.(Umetani and Freiser, 1987) These 4- acylpyrazolones have been reported to be more efficient extractants for metals in strong acidic solutions and cheaper than the widely used 4,4,4 - triflouro 1-(2-thenoyl)-1-3- butadiene, ($C_4H_{10}SCOCH_2COCF_3$)(Umetani and Matsui, 1992). Thus the 4-acyl pyrazolone ligands have been used in the spectrophotomeric determination of metals in trace amounts.(Ogwuegbu and Oforka, 1994, Santhi et al., 1994, Torkestani et al., 1996) Recently a rash of publications and communications have appeared in literature showing the ability of these ligands to form stable and hydrophobic complexes with characteristic brilliant colours.(Casas et al., 2007, Emeleus et al., 2001, Ivanova et al., 2006, Umetani et al., 2000, Uzoukwu et al., 2000, Uzoukwu and Mbonu, 2005, Uzoukwu and Gloe, 2003, Uzoukwu et al., 2004) Such complexation reactions are widely used in analytical chemistry for the determinations and isolations of almost all metal ions. This is due to quite a number of valuable properties of these ligands such as high extracting ability, intense colour of the complexes formed and low solubility of the complexes in some solvents.(Ivanova et al., 2006) The selectivity of these ligands for metal ions is dependent on the properties of the ligand anion which in turn depends on the nature of the substituents in the 4-acyl position of the pyrazole ring.(Okafor, 1982, Umetani et al., 2000, Uzoukwu, 1992) These substituents may contain donor atoms which are very versatile, due to the possibility of deeply changing the steric and electronic features of the compound on substitution at the 4-acyl position.(Uzoukwu, 1992) This present effort is geared towards investigating the effect of the 4-acyl substituents on the stability of the carbonyl and metal oxygen bonds of some 1-phenyl-3-methyl-4-acyl pyrazol-5-ones and their divalent metal chelates.

2. Experimental

All reagents used were analytical grade and needed no further purification.

2.1 Synthesis of the Ligands

The ligands were synthesized by methods described elsewhere.(Okafor, 1981)

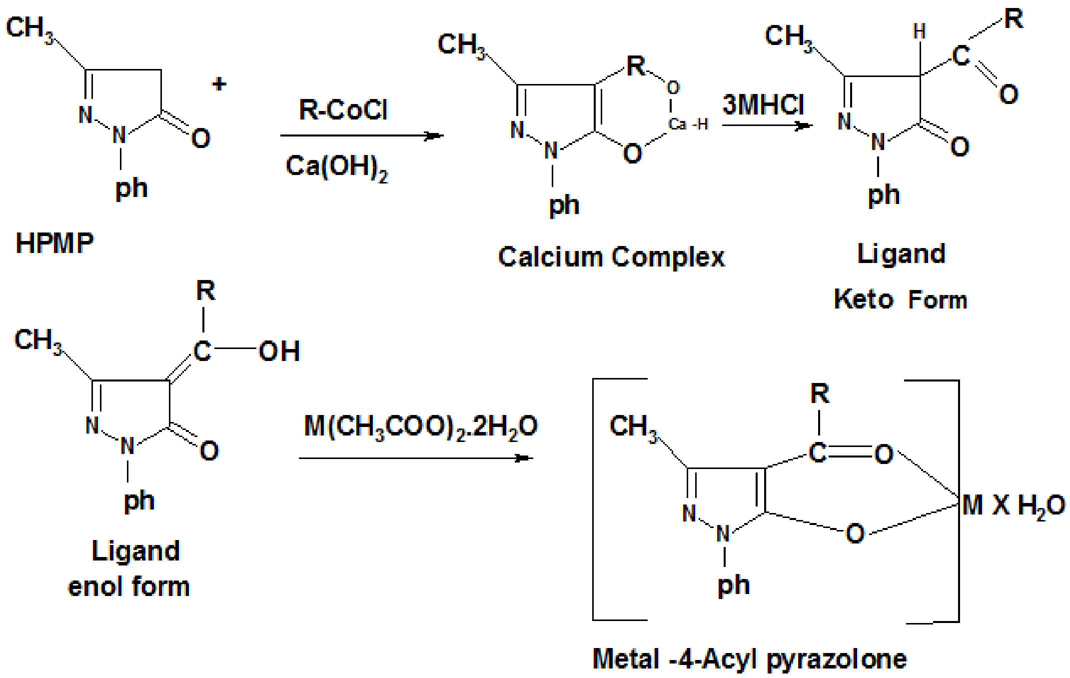
2.2 Synthesis of the metal complexes.

A 75ml aqueous solution of the metal (II) acetate ($Mg^{2+},Co^{2+}, Cu^{2+}, Zn^{2+}$) $M(CH_3COO_2)_2\ .4H_2O$) containing 5mmol was prepared and warmed. This was added with stirring to a hot ethanol solution (75ml) containing 10mmol of the ligand anion. The mole ratio of the metal ligand interaction was 1:2. The complex precipitated out of solution instantly and was washed with 2:1 water-ethanol solution . The product was dried in air and stored in a desiccator.

2.3 Physical Measurements

The melting point and dissociation temperatures were determined in an electrothermal melting point apparatus. The molar conductance values of the complexes in DMF were obtained at 27^0C with the Jenway Digital Conductivity meter (J4500). The electronic spectra of the compounds was obtained in a Jenway (J6405) UV-Visible spectrophotometer and the infrared spectral measurements between 4000 - 400cm^{-1} was carried out with a Perkin-Elmer Fourier Transform Infrared Spectraphotometer. (Model 100)

Reaction Scheme



3. Results and Discussion

The micro - analytical data presented in Table 1 show that in aqueous solution , the mode of interaction of the metal ions (Mg^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}) and the ligands is in the ratio of 1:2. The complexes are therefore bischelates associated with two (2) molecules of water of crystallisation from the aqueous media except for the zinc complexes which do not contain any water of crystallisation . Since the ligands have been known to exist as keto-enol tautomers(Ivanova et al., 2006). The displacement of the hydrogen atom of the keto-enol tautomer leads to the formation of the metal complexes.

Table 1.0: Microanalytical data for the Ligands and Metal Chelates

Compound	**Molecular Formular**	**colour**	**M .p t**	**Yield %**	**Calculated (%)**			**Found (%)**		
					C	H	N	C	H	N
Hpmap	$C_{12}H_{12}O_2N_2$	white	57	52	66.65	5.60	12.96	66.58	5.57	12.91
Hpmprp	$C_{13}H_{14}O_2N_2$	yellow	62	75	67.81	6.13	12.17	67.51	5.80	12.17
Hpmbup	$C_{14}H_{16}O_2N_2$	brown	77	89	68.83	6.60	11.47	68.68	6.7	11.30
$Mg(pmap)_2$. $2H_2O$	$MgC_{24}H_{28}O_6N_4$	white	202	78	56.91	5.17	11.06	57.31	5.08	11.04
$Mg(pmprp)_2$. $2H_2O$	$MgC_{26}H_{32}O_6N_4$	yellow	183	55	61.52	5.36	11.03	61.91	5.41	10.68
$Mg(pmbup)_2$. $2H_2O$	$MgC_{28}H_{36}O_6N_4$	white	160	60	62.78	5.83	10.46	62.93	6.0	10.32
$Co(pmap)_2$. $2H_2O$	$CoC_{24}H_{28}O_6N_4$	Pink	166	59	54.88	4.99	10.66	54.69	4.87	10.62
$Co(pmprp)_2$. $2H_2O$	$CoC_{26}H_{32}O_6N_4$	Pink	159	75	57.2	5.7	9.6	57.4	5.7	9.17
$Co(pmbup)_2$. $2H_2O$	$CoC_{28}H_{36}O_6N_4$	Pink	147	58	56.4	5.5	10.2	56.25	5.7	10.3
$Cu(pmap)_2$. $2H_2O$	$CuC_{24}H_{28}O_6N_4$	Green	257	72	58.11	4.90	11.30	58.21	4.82	11.22
$Cu(pmprp)_2$. $2H_2O$	$CuC_{26}H_{32}O_6N_4$	Green	248	67	62.99	5.29	11.30	62.96	5.37	11.28
$Cu(pmbup)_2$. $2H_2O$	$CuC_{228}H_{36}O_6N_4$	D.Green	246	73	64.21	5.77	10.70	63.80	5.53	10.59
$Zn(pmap)_2$. $2H_2O$	$ZnC_{24}H_{28}O_6N_4$	White	191	86	54.21	4.93	10.53	54.30	4.86	10.47
$Zn(pmprp)_2$	$ZnC_{26}H_{28}O_4N_4$	Yellow	170	58	65.20	5.84	10.14	65.20	6.20	10.06
$Zn(pmbup)_2$	$ZnC_{28}H_{32}O_4N_4$	B.White	145	62	70.88	9.11	6.34	70.97	8.34	6.26

Legend pmap= 4-acetyl pyrazolone-5, pmprp = 4- propionyl pyrazolone-5, pmbup = 4 –butyryl pyrazolon-5

3.1 Solubility

The solubility data presented in Table 2 show that all the ligands were insoluble in aqueous solution, while all the metal complexes were hydrophobic, indicating that the distribution of the complexes from the aqueous media into the organic media such as chloroform ($CHCl_3$) ,diethylether ($CH_3CH_2OCH_2CH_3$) and carbontetrachloride (CCl_4) ,in which they are slightly soluble is favourable. All the complexes showed remarkable solubility in dimethylformamide (DMF) and dimethylsulphoxide (DMSO). These two solvents have lone pairs of electrons for donation, which probably completed the octahedron geometry in the structure of the complexes and thus reducing the ionic character of the complexes if any. This observation suggests that these two solvents could be efficient synergist in the extraction of Mg (II), Co (II) Cu (II) and Zn (II) ions from aqueous media.

3.2 Conductivity

The molar conductance of 0.001M solutions of the metal complexes shown in Table 3 indicate that the ligands form non-ionic complexes with the metal ions.

Table 2; Solubility Data for the Ligands and Metal Complexes

Solvents	Hm pap	Hm prp	Hm bup	Mg pap	Mg prp	Mg bup	Co pap	Co prp	Co bup	Cu pap	Cu prp	Cu Bup	Zn pap	Zn prp	Zn bup
Water	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I
Methanol	SP	SP	SP	S	SP	SP	SP	SP	I	SP	S	S	I	I	I
Ethanol	SP	SP	SP	SP	SP	SP	SP	SP	I	SP	S	S	I	I	I
D.Ether	VS	VS	VS	VS	S	SP	I	S	SP	I	VS	VS	I	I	S
Acetone	VS	VS	VS	VS	S	SP	S	SP	SP	SP	SP	VS	VS	SP	SP
Dioxane	VS	VS	VS	S	S	S	SP	SP	S	SP	SP	SP	SP	SP	S
THF	VS	VS	VS	VS	SP	S	VS	SP	VS	S	VS	VS	I	VS	S
CCL_4	VS	VS	VS	VS	S	SP	SP	SP	SP	SP	SP	VS	SP	SP	SP
Hexane	VS	VS	VS	VS	I	I	I	SP	SP	SP	VS	SP	SP	SP	SP
Pyridine	VS	VS	VS	S	VS	S	VS	VS	VS	VS	VS	VS	SP	VS	VS
Benzene	VS	VS	VS	SP	SP	I	I	SP	SP	I	S	S	SP	SP	SP
DMF	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS
DMSO	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS	VS

Legend: VS=Very Soluble,S= Soluble, SP= Sparingly Soluble, I= Insoluble

Table 3.0: Molar Conductance Values for the Metal Complexes

Compound	Conc (mg/l)	Molar Con(μohm^{-1}m^{-1})
$Mg(PMAP)_2 .2H_20$	0.012	8.6
$Mg(PMPRP)_2 .2H_20$	0.015	9.2
$Mg(PMBUP)_2 .2H_20$	0.013	7.1
$Co(PMAP)_2 .2H_20$	0.01	4.8
$Co(PMPRP)_2 .2H_20$	0.013	6.9
$Co(PMBUP)_2 .2H_20$	0.012	7.2
$Cu(PMAP)_2 .2H_20$	0.01	21.5
$Cu(PMPRP)_2 .2H_20$	0.013	18.4
$Cu(PMBUP)_2 .2H_20$	0.17	9.2
$Zn(PMAP)_2$	0.026	6.7
$Zn(PMPRP)_2$	0.012	1.6
$Zn(PMBUP)_2$	0.018	2.5

3.3 Elecronic Spectra

The U.V-Visible spectra of the ligands and metal complexes are presented in Table 4. The spectra of both the ligands and complexes showed absorption bands near 250 nm and 296 nm in the ultraviolet region of the electromagnetic spectra, resulting from intra-ligand $\Pi \leftarrow \Pi^*$ transitions. It is evident from the data that the spectra of the metal complexes and that of their corresponding ligands are similar. The λ_1 and λ_2 of the ligands remain either unchanged in the metal complexes or suffer slight bathochromic shifts resulting from complex formation. Similar observation has been reported previously.(Okafor, 1980, Okafor and Uzoukwu, 1991, Uzoukwu et al., 1993, Uzoukwu et al., 1998b) It was suggested in these reports that the Π- bonding system in the ligand is preserved in the metal complexes. No d-d transitions were observed. This may be due to constraints imposed by the selection rule which forbids transitions where the azimuthal quantum numbers are the same or the bands were obscured in the more intense $\Pi \leftarrow \Pi^*$ bands. There was no interaction between the Π – bonding system of the ligand and the metal ions. The coordination between the metal ions and the ligand anions was therefore through σ – bond formation between the metal ions and the oxygen atoms of the two carbonyl groups of the ligand.(Uzoukwu, 1990) This was achieved by deprotonation of the enolic hydroxyl group of the ligand and acceptance of an electron pair from the oxygen atom of the second carbonyl group.

3.4 Infrared Spectra

The Infrared spectroscopic properties of metal (II) chelates of 4 – acyl pyrazolon-5 ligands like the 4-acetyl, 4 – triflouroacetyl, 4 – butyryl, 4 – benzoyl and 4 – trichloroacetyl ,4-sebacoyl and 4-valeroyl derivatives have been extensively studied.(Okafor, 1980, Uzoukwu et al., 1993, Uzoukwu et al., 1998b, Uzoukwu, 1995, Uzoukwu et al., 1996) We have extended the investigation to substituted 4-acyl pyrazolon-5 derivatives by studying the effect on the chelate ring by varying the nature (alkyl, and aryl) and length of the 4-acyl substituent. The selected observed frequencies presented in Table 5 have been assigned by comparing with those of previous reports.(Okafor, 1981, Okafor, 1982, Uzoukwu, 1992) The broad absorption bands appearing near 3469cm^{-1} – 3401cm^{-1} have been attributed to the υ –OH of coordinated water or lattice water molecules present in all the complexes except the Zn(II) complexes. The broad band centered around 3062cm^{-1} and 3065cm^{-1} in the HPMAP and HPMBUP spectra, which appeared as a weak band around 2953cm^{-1} in the spectrum of HPMPRP are assigned to vibrational frequency modes of the enolic OH. This is absent in the spectra of the metal complexes , indicating the deprotonation of the OH group during chelation. This observation further supports the earlier suggestion that the only interaction between the metal(II) ions and the ligand anions resulted from a σ – bond between the metal ions and the oxygen atoms of the keto-enol tautomer of the ligand. The data in Table 5 also show vibrational frequency bands (υ –C=O) of the ligand between 1619cm^{-1} and 1627cm^{-1} appearing near 1639cm-1, 1623cm^{-1}, 1607cm^{-1} and 1615cm^{-1} in the spectra of the Mg (II), Co (II), Cu (II) and Zn (II) complexes respectively. These observation further suggest the involvement of the carbonyl groups in bonding. Previous works reported similar results (Casas et al., 2007, Mirza and Nwabue, 1981, Okafor, 1981). The effects of the 4-acyl substituent on the carbonyl and metal – oxygen bond have been investigated and the spectral data presented in Table 6.Th results indicate that increasing the length of the carbon chain of the substituent at the 4-acyl position showed increased stability of the C=O bond for the Mg(II), Co(II), and Cu(II) ions and a decrease in the stability of the C=O bond for the Zn(II) chelates. The reason for this reverse trend in the case of Zn(II) chelates is not yet clear since increase in the carbon chain length of the substituent at the 4 – acyl position normally leads to increase in electron density around the C=O bond and this should transmit to increased stability of the bond. Electronic and steric hinderances have been suggested as a possible reason for the anomaly. Similar results was reported for the Ni(II) complexes of some 1 – phenyl -3- methyl – 4-acyl pyrazolon – 5 ligands.(Uzoukwu, 1990) The carbonyl stretching frequencies for the transition metal complexes followed the trend Co > Zn > Cu which does not correspond to the irving Williams stability order for transition metal complexes.($Cu^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+} > Zn^{2+}$). The data on the effects of the alkyl substituent on the C = C bond stability presented in Table 6, shows that there were little or no effects by increasing the length of the carbon chain of the alkyl substituents at the 4-acyl position on the stability of the C = C bonding system. The infrared vibrational frequency bands resulting from metal – oxygen vibrations of the chelate ring are shown in Table 5 and comparing with similar studies,(Uzoukwu, 1992) vibrational frequency modes between 445cm^{-1} and 497cm^{-1} have been assigned to M – O bond. The effect of the length of the alkyl carbon atoms substituted at 4-acyl position on the stability of the M – O bond was investigated and the data also presented in table 6.The results indicate that the stability of the M –O bond decreased with increase in the lengths of the carbon atom of the alkyl substituent at the 4 – acyl position for the four metal ions. The reason for this observation has not been properly understood as the result indicated a decrease in electron density around the M – O bond as the length of the alkyl carbon atom increased, although previous workers,(Okafor, 1982, Okafor et al., 1990, Umetani et al., 2000, Uzoukwu, 1992) have always observed a reverse trend in the stability of the C=O and M=O bonds on increasing the length of the alkyl carbon atom substituted at the 4 – acyl position of the pyrazole ring system.

Table 4.0: Electronic Spectral Data of the Ligands and their metal complexes

COMPOUND	Λ_1 max(nm)	E_1(mol^{-1}cm^{-1})	$\Lambda_2$max(nm)	E_2(mol^{-1}cm^{-1})
HPMAP	250	1.0 X 10^3	279	4.9 X1 0^4
HPMBUP	250	7.4 X 10^3	280	5.5 X 10^4
HPMPRP	252	9.6 X 10^3	280	5.8 X 10^3
$Mg(PMAP)_2.2H_2O$	250	4.2 X 10^3	287	1.0 X 10^4
$Mg(PMPRP)_2.2H_2O$	258	3.6 X 10^3	285	3.0 X 10^4
$Mg(PMBUP)_2.2H_2O$	259	6.2 X 10^3	285	3.8 X 10^4
$Co(PMAP)_2.2H_2O$	257	1.4 X 10^3	287	1.0 X 10^4
$Co(PMPRP)_2.2H_2O$	254	1.43 X 10^4	294	3.6 X 10^4
$Co(PMBUP)_2.2H_2O$	256	5.6 X 10^3	293	2.6 X 10^4
$Cu(PMAP)_2.2H_2O$	257	9.2 X 10^3	291	2.6 X 10^3
$Cu(PMPRP)_2.2H_2O$	258	4.2 X 10^3	291	3.2 X 10^4
$Cu(PMBUP)_2.2H_2O$	258	6.7 X 10^3	293	4.6 X 10^4
$Zn(PMAP)_2$.	262	3.7 X 10^3	292	3.2 X 10^4
$Zn(PMPRP)_2$	251	4.3 X 10^3	296	2.6 X 10^3
$Zn(PMAP)_2$.	252	3.1 X 10^3	292	5.6 X 10^4

Table 5.0 Infrared Spectral Data for the ligands and Metal Complexes

Coumpound	V-O-H	V-C = O	V_{as} C = O	V_{as} C =O	V-M-O
HPMAP	3468br	1619vs		1500m	
HPMPRP	3469br	1626vs		1504s	
HPMBUP	3470br	1627s		1499s	
$Mg(PMAP)_2.2H_2O$	3470br		1634s	1512br	493s
$Mg(PMBUP)_2.2H_2O$	3430br		1643vs	1512s	470vs
$Mg(PMPRP)_2.2H_2O$	3429br		1639vs	1513s	470s
$Co(PMAP)_2.2H_2O$	3573br		1623vs	1485vs	448s
$Co(PMBUP)_2.2H_2O$	3401br		1626vs	1509vs	455vs
$Co(PMPRP)_2.2H_2O$	3421br		1624vs	1509vs	448s
$Cu(PMAP)_2.2H_2O$	3468br		1606vs	1497s	477m
$Cu(PMBUP)_2.2H_2O$	3468br		1609vs	1500vs	489vs
$Cu(PMPRP)_2.2H_2O$	3468br		1607vs	1497s	497s
$Zn(PMAP)_2.2H_2O$	3574sh		1623vs	1488s	447m
$Zn(PMBUP)_2$	-		1615vs	1508s	467vs
$Zn(PMPRP)_2$	-		1619vs	1509s	459s

Legend: br = broad; vs = very strong; s = strong; m = medium; sh = sharp

Table 6.0: Effect of 4-acyl Substituents on the Carbonyl and metal Oxygen Stretching frequencies of the ligands and their metal complexes.

	V_{as} C =C (cm^{-1})			V_{as} C =O (cm^{-1})			V – M – O (cm-^{1})		
	HPMAP	HPMPRP	HPMBUP	HPMAP	HPMPRP	HPMBUP	HPMAP	HPMPRP	HPMBUP
Ligand	1500	1504	1499	1619	1626	1627	-	-	-
Mg	1512	1513	1512	1634	1639	1643	493	470	470
Co	1485	1509	1509	1623	1624	1626	448	448	455
Cu	1497	1497	1500	1606	1607	1609	497	497	489
Zn	1488	1509	1508	1625	1619	1625	447	459	467

4. Conclusion

The microanalytical data showed that the metal (II) complxes of the 4-acetyl , 4-butyryl and 4-proponyl ligands are bischelates with two molecules of water of crystallisation with the exception of the zinc chelates . The U.V and IR spectral data confirmed that the Π bond interaction is not present in any of the complexes but suggested a σ- bond interaction between the metal ions and the deprotonated hydroxyl group of the enol tautomer of the ligand. Increase in the length of the substituent at the 4-acyl position led to increased stability of the C=O bond but decreased stability of the M-O bond. The C=O Stretching frequency for the transition metal chelates did not follow the irving Williams stability order for transition metal complexes

REFERENCES

AKAMA, Y., SATO, K., UKAJI, M., KAWATA, T. & KAJITANI, M. (1985) Studies on extraction of copper (II) with 1-phenyl-3-methyl-4-acyl-5-pyrazolone. *Polyhedron,* **4,** 59-63.

AKAMA, Y., YOKOTA, H., SATO, K. & NAKAI, T. (1986) Studies on extraction of manganese (II) with 1-phenyl-3-methyl-4-acyl-5-pyrazolone. *Talanta,* 33**,** 288-290.

CASAS, J. S., GARCÍA-TASENDE, M. S., SÁNCHEZ, A., SORDO, J. & TOUCEDA, Á. (2007) Coordination modes of 5-pyrazolones: A solid-state overview. *Coordination Chemistry Reviews,* 251**,** 1561-1589.

CORONEL, F. T., MAREVA, S. & YORDANOV, N. (1982) Extraction of uranium (IV) from phosphoric acid solutions with 1-phenyl-3-methyl-4-benzoylpyrazolone-5 (PMBP). *Talanta,* 29**,** 119-123.

EMELEUS, L. C., CUPERTINO, D. C., HARRIS, S. G., OWENS, S., PARSONS, S., SWART, R. M., TASKER, P. A. & WHITE, D. J. (2001) Diazopyrazolones as weak solvent extractants for copper from ammonia leach solutions. *Journal of the Chemical Society, Dalton Transactions***,** 1239-1245.

HASANY, S. & QURESHI, I. (1977) Extraction of group IB, IIB and III-VA elements with 1-phenyl-3-methyl-4-trifluoroacetyl-pyrazolone-5. *Journal of Radioanalytical and Nuclear Chemistry,* 40**,** 29-39.

IVANOVA, B., CHAPKANOV, A., ARNAUDOV, M. & PETKOV, I. (2006) Tautomerism in 1‐Phenyl‐3‐Substituted Pyrazol‐5‐ones: FT‐Infrared Spectral Analysis and Ab Initio Calculations. *Spectroscopy letters,* 39**,** 1-12.

JYOTHI, A. & RAO, G. (1990) Solvent extraction behaviour of lanthanum (III), cerium (III), europium (III), thorium (IV) and uranium (VI) with 3-phenyl-4-benzoyl-5-isoxazolone. *Talanta,* 37**,** 431-433.

KALAGBOR, A., UZOUKWU, B. & CHUKWU, U. (2011) Extraction of molybdenum (VI) with 4-adipoyl and 4-sebacoyl derivatives of bis (1–phenyl-3methylpyrazolone-5) in acid media. *Nature and Science,* 9**,** 37-42.

MIRZA, M. & NWABUE, F. (1980) Studies on the Extraction of Ti (IV), Ce {IV), Th (IV) and U (VI) with 1-Phenyl-3-methyl-4-benzoyl-pyrazole-5-one from Different Mineral Acids. Separation of Thorium from Titanium, Uranium and Rare Earths. *Radiochimca Acta,* 27**,** 47-50.

MIRZA, M. & NWABUE, F. I. (1981) 1-Phenyl-3-methyl-4-benzoylpyrazol-5-one as a group-extraction reagent for spectrophotometric determination of trace elements. *Talanta,* 28**,** 49-53.

NAVRATIL, O. & JENSEN, B. (1970) Solvent extraction of Hf (IV) and Zr (IV) with some 1-phenyl-3-methyl-4-acylpyrazolones-5. *Journal of Radioanalytical Chemistry,* 5**,** 313-322.

OGWUEGBU, M. & OFORKA, N. (1994) 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,* 34**,** 359-367.

OKAFOR, E. C. (1980) Synthesis of Some New Tris Rare Earth Chelates of 12phenyl232methyl242benzoyl2pyrazolone25 and Their UV, IR and NMR Spectral Studies. *J Inorg Nucl Chem,* 42, 1155.

OKAFOR, E. C. (1981) The metal complexes of heterocyclic β-diketones and their derivatives—V. The synthesis, structure and ir spectral studies of metal (II) complexes of 1-phenyl-3-methyl-4-acetyl-pyrazolone-5 (HPMAP). *Spectrochimica Acta Part A: Molecular Spectroscopy,* 37**,** 939-944.

OKAFOR, E. C. (1982) Observations on 1-phenyl-3-methyl-4-trifluoroacetylpyrazolone-5, a promising extracting agent. *Talanta,* 29**,** 275-278.

OKAFOR, E. C., UZOUKWU, A. B., HITCHCOCK, P. B. & SMITH, J. D. (1990) Pyrazolonato complexes of uranium. Crystal structures of bis-oxobis (1-phenyl-3-methyl-4-acetylpyrazol-5-onato) aquouranium (VI) and Bis-oxobis (1-phenyl-3-methyl-4-benzoylpyrazol-5-onato (propanol) uranium (VI). *Inorganica chimica acta,* 172**,** 97-103.

OKAFOR, E. C. & UZOUKWU, B. A. (1990) Extraction of Fe (III) and U (VI) with 1-Phenyl-3-methyl-4-acyl-pyrazolones-5 from Aqueous Solutions of Different Acids and Complexing Agents. Separation of Fe (III) from U (VI). *Radiochimca Acta,* 51**,** 167-172.

OKAFOR, E. C. & UZOUKWU, B. A. (1991) Introducing a New bis (β-Diketone): Syntheses, UV-Visible, IR, 1H and 13C NMR Spectral Studies of 4-Sebacoyl-bis (1-phenyl-3-methyi-pyrazolone-5)(H2PMSP) and Its, U (VI), Fe (III) and Ca (II) Complexes. *Synthesis and reactivity in inorganic and metal-organic chemistry,* 21**,** 825-844.

OZAKI, T., MIYAZAKI, S., UMETANI, S., KIHARA, S. & MATSUI, M. (1989) Solvent extraction of zinc with 1-(2′-chlorophenyl)-3-methyl-4-aroyl-5-pyrazolones. *Analytica chimica acta,* 226**,** 187-192.

SANTHI, P., REDDY*, M., RAMAMOHAN, T., DAMODARAN, A., MATHUR, J., MURALI, M. & IYER, R. (1994) SYNERGISTIC SOLVENT EXTRACTION OF TRIVALENT LANTHANIDES AND ACTINIDE BY MIXTURES OF 1-PHENYL-3-METHYL-4-BENZOYL-PYRA2ALONE-5 AND NEUTRAL OXO-DONORS. *Solvent extraction and ion exchange,* 12**,** 633-650.

TORKESTANI, K., BLINOVA, O., ARICHI, J., GOETZ-GRANDMONT, G. & BRUNETTE, J. (1996) Synergistic extraction of copper (II) and other divalent metals with 3-phenyl-4-acylisoxazol-5-ones and 1-phenyl-3-methyl-4-acylpyrazol-5-ones in the presence of tri-n-octylphosphine oxide in toluene. *Solvent extraction and ion exchange,* 14**,** 1037-1056.

UMETANI, S. & FREISER, H. (1987) Mixed-ligand chelate extraction of lanthanides with 1-phenyl-3-methyl-4-(trifluoroacetyl)-5-pyrazolone and some phosphine oxide compounds. *Inorganic Chemistry,* 26**,** 3179-3181.

UMETANI, S., KAWASE, Y., LE, Q. T. & MATSUI, M. (2000) Acylpyrazolone derivatives of high selectivity for lanthanide metal ions: effect of the distance between the two donating oxygens. *Journal of the Chemical Society, Dalton Transactions***,** 2787-2791.

UMETANI, S. & MATSUI, M. (1992) Solvent extraction of alkaline-earth metals with 4-acyl-5-pyrazolones and polydentate phosphine oxides. *Analytical Chemistry,* 64**,** 2288-2292.

UZOUKWU, A. B., AL-JUAID, S. S., HITCHCOCK, P. B. & DAVID SMITH, J. (1993) The synthesis and crystal structures of 1-phenyl-3-methyl-4-butanolypyrazol-5-one and of two pyrazolonato complexes of iron. *Polyhedron,* 12**,** 2719-2724.

UZOUKWU, B., GLOE, K. & DUDDECK, H. (1998a) Extraction of uranium (VI) and vanadium (V) with 4-adipoyl and 4-sebacoyl derivatives of bis (1-phenyl-3-methyl-pyrazolone-5) and effect of decanol on the distribution behaviour of these metal ions. *Solvent extraction and ion exchange,* 16**,** 751-774.

UZOUKWU, B., GLOE, K. & DUDDECK, H. (1998b) Metal (II) Complexes of 4-Acylbis (Pyrazolone-5): Synthesis and Spectroscopic Studies. *Synthesis and Reactivity in Inorganic and Matel-Organic Chemistry,* 28**,** 207-221.

UZOUKWU, B., GLOEB, K. & ADIUKWU, P. (2000) Molybdenum (VI), Uranium (VI) and Vanadium (V) Complexes of 4-Acylbis (L-Phenyl-3-Methylpyrazolone-5): Synthesis and Spectroscopic Characterization. *Sythesis and Reactivity in Inorganic and Matel-Organic Chemistry,* 30**,** 433-443.

UZOUKWU, B. & MBONU, J. (2005) 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 extraction and ion exchange,* 23**,** 759-771.

UZOUKWU, B. A. (1990) Metal Complexes of β-Diketones: Synthesis, Ultraviolet and Infrared Spectral Studies of Nickel (II) Complexes of 1-Phenyl-3-methyl-4-acyl-pyrazolone-5. *Synthesis and reactivity in inorganic and metal-organic chemistry,* 20**,** 1071-1084.

UZOUKWU, B. A. (1992) Electronic and vibrational studies of copper (II) complexes of 1-phenyl-3-methyl-4-acylpyrazolones-5. *Spectrochimica Acta Part A: Molecular Spectroscopy,* 48**,** 1021-1022.

UZOUKWU, B. A. (1995) Spectrophotometric studies on 4-acyl derivatives of 1-phenyl-3-methylpyrazolone-5 in various solvents. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,* 51**,** 1081-1082.

UZOUKWU, B. A., ADIUKWU, P., AL-JUAID, S. S., HITCHCOCK, P. B. & SMITH, J. D. (1996) Pyrazolonato complexes of lead. Crystal structures of bis (1-phenyl-3-methyl-4-acetyl pyrazolonato) lead (II) and bis (1-phenyl-3-methyl-4-butanoylpyrazolonato) lead (II). *Inorganica chimica acta,* 250**,** 173-176.

UZOUKWU, B. A. & GLOE, K. (2003) Extraction studies and synthesis of molybdenum (VI) complexes of 4-adipoyl and 4-sebacoyl derivatives of bis (1-phenyl-3-methyl-pyrazolone-5). *INDIAN JOURNAL OF CHEMISTRY SECTION A,* 42**,** 2727-2734.

UZOUKWU, B. A., GLOE, K., MENZEL, M. & WAWRZYNIAK, K. (2004) Syntheses and^ 1^ 1^ 9Sn Mossbauer spectral characterization of tin (IV) complexes of 4-acyl-1-phenyl-3-methylpyrazolones-5 and molecular modelling of 4-acetyl-1-phenyl-3-methylpyrazolone-5. *INDIAN JOURNAL OF CHEMISTRY SECTION A,* 43**,** 701-705.

The IISTE is a pioneer in the Open-Access hosting service and academic event management. The aim of the firm is Accelerating Global Knowledge Sharing.

More information about the firm can be found on the homepage:
http://www.iiste.org

CALL FOR JOURNAL PAPERS

There are more than 30 peer-reviewed academic journals hosted under the hosting platform.

Prospective authors of journals can find the submission instruction on the following page: http://www.iiste.org/journals/ All the journals articles are available online to the readers all over the world without financial, legal, or technical barriers other than those inseparable from gaining access to the internet itself. Paper version of the journals is also available upon request of readers and authors.

MORE RESOURCES

Book publication information: http://www.iiste.org/book/

Academic conference: http://www.iiste.org/conference/upcoming-conferences-call-for-paper/

IISTE Knowledge Sharing Partners

EBSCO, Index Copernicus, Ulrich's Periodicals Directory, JournalTOCS, PKP Open Archives Harvester, Bielefeld Academic Search Engine, Elektronische Zeitschriftenbibliothek EZB, Open J-Gate, OCLC WorldCat, Universe Digtial Library , NewJour, Google Scholar