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SYNTHESIS AND SPECTROSCOPIC CHARACTERISATION OF COBALT (II) COMPLEXES OF 1-PHENYL-3-METHYL-4-ACYL PYRAZOL-5-ONE DERIVATIVES

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ABSTRACT

The complexes of cobalt (II) with 4-acetyl (HPMAP), 4-benzoyl (HPMBP), 4-butyryl (HPMBUP), 4-capyroyl (HPMCP), 4-propionyl (HPMPRP) and 4-palmitoyl (HPMPP) derivatives of 1-phenyl-3-methyl pyrazol-5-ones has been synthesized. Characterisation was done by elemental analysis, UV, IR and conductivity measurements. The ligands behaved like bidentate enols, forming neutral chelates with cobalt (II) ions bonding through the keto oxygen or enolic hydrogen in the carbonyl group of the ligands keto-enol tautomer. The chelates were found to be neutral bis chelates having general molecular formular $ML_2.XH_2O$, Where M = Co, L is the 4-acyl pyrazolone anion, X is the No. of molecules of adducted water. The infrared spectra of the ligands and cobalt (II) complexes were measured between 4000 – 400 cm^{-1} and assignments proposed for the observed frequencies. The effect of 4-acyl substituents on the carbonyl stretching frequencies of the metal complexes were investigated and results showed that the stability of the C=O and CO-M bond depends on the nature of the alkyl substituent on the 4-acyl position.

Key words: Cobalt (II) complex, 1-Phenyl-3-methyl-4-acyl pyrazol-5-one.

INTRODUCTION

Research on β-diketones and their metal complexes has been stimulated by a number of reasons, such as their interesting applications in metal extraction[1,2]. NMR shift reagents[3,4]. and laser technology[5]. Studies have shown that 4-acyl pyrazolones, are suitable for practical applications in solvent extraction of metals[6-8], hydrometallurgy[9] and water treatment[10].

Apart from their application in metal extraction, 4-acyl pyrazolones have shown strong antifungal antihistamic and analgesic properties[11,12]. Attempt at using other

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derivatives of the pyrazolone moiety in construction mixed ligand resins for trapping heavy metals chromatographically have been made[13,15]. Application of metal 4-acyl pyrazolones as NMR shift reagents and laser materials have not received considerable attention because of the absence of sufficient spectroscopic data on these class of compounds. The present study looks at the interaction between Co (II) ion and these chelating agents in solution.

EXPERIMENTAL

All reagents used were of analytical grade and did not require any further purification.

Synthesis of the ligands

The synthesis was carried out using a modified Jensen's method[14]. About (8.5 g) of 1-phenyl-3-methyl pyrazolone (HPMP) was dissolved in 100 cm^3 of Dioxane in a 1 Litre three necked flask fitted with an electric stirrer and a reflux condenser by warming. The dioxane solution was allowed to cool to room temperature before 10 g of $Ca(OH)_2$ was added and the mixture stirred for 30 minutes. Acetyl chloride (3.5 cm^3) was added dropwise within 3 minutes. The reaction mixture stirred for 1 hour with low application of heat. The resulting orange mixture was then poured into a chilled 3 M HCl (500 cm^3) solution with vigorous stirring. The reaction mixture was later kept in a refrigerator until pinkish crystals separated. The crystals were filtered off, washed with distilled water and recrystalized from aqueous ethanol to give white crystals. The crystals were dried in air and stored in a desiccators.

The propionyl, benzoyl, butyryl, capyroyl and palmitoyl derivatives of the ligands were also synthesized using similar methods with equimolar quantities of 1-phenyl-3-methyl pyrazolone-5 and the corresponding acyl chlorides.

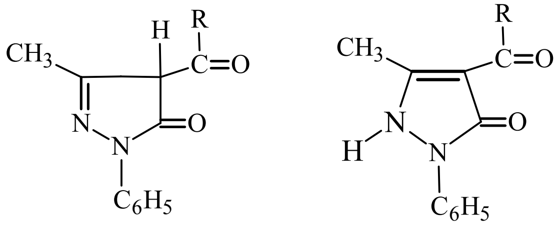
Synthesis of cobalt (II) complexes

A 75 mL aqueous solution of cobalt (II) acetate $Co(CH_3COO)_2 . 4H_2O$ containing 5 mM (1.25 g) of the acetate was prepared and warmed. This was added to 75 mL of a hot ethanol solution (45^{o}C) containing 10 mM of the ligand. The complex precipitated out of the solution instantly and was washed with 2 : 1 water-ethanol solution. The resulting product was dried in air and stored in a desiccators.

RESULTS AND DISCUSSION

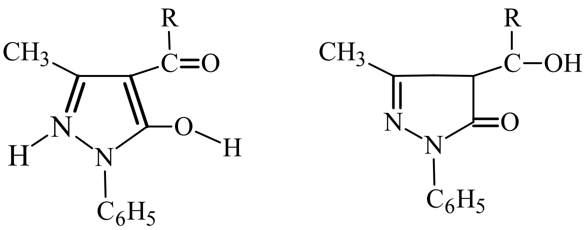
Structure of ligands and complexes

Some 1-phenyl-3-methyl-4-acyl pyrazolone-5 have been synthesized and the IR spectral measurements (HPMAP, HPMBP, HPMBUP, HPMCP, HPMPRP, HPMPP), showed that the ligands may exist in four tautomeric forms as shown in Fig. 1. R = HPMAP (1-phenyl-3-methyl-4-acetyl pyrazolone-5), HPMBP (1-phenyl-3-methyl-4-benzoyl pyrazolone-5), HPMBUP (1-phenyl-3-methyl-4-butyryl pyrazolone-5), HPMCP (1-phenyl-3-methyl-4-caproyl pyrazolone-5), HPMPRP (1-phenyl-3-methyl-4-propionyl pyrazolone-5), HPMPP(1-phenyl-3-methyl-4-butyryl pyrazolone-5). The results from infrared spectral analysis showed that only three forms of the ligand may have been isolated from aqueous ethanol and they are the forms in Fig. **1a**, **1c** and **1d** above. The two enolic tautomeric forms in 1c and 1d have been reported to be in resonance[15], while the possibility of an amino-diketo form of the ligand (1b) has been eliminated by the absence of bands between 3100 – 3500 cm^{-1} in the anhydrous form of the ligand[16].



(a) **(b)**

Keto forms



(c) **(d)**

Enol forms

Fig. 1: Tautomeric forms of the ligand

Physical and analytical data

The microanalytical data are listed in Tables 1 and 2. The elemental analysis data in Table 1 shows that in aqueous solution, the mode of interaction of the Co (II) ion and the ligands is in the ratio of 2 : 1. The complexes are therefore bischelates associated with molecules of water of crystallization from aqueous medium. They conform to the general formular ML_2XH_2O where M = Co, L = 4-acylpyrazolone-5 anion and X = 0,1 or 2. The molar conductance values 0.001 M solutions of the metal complexes in DMF at 27^{o}C were all bellow 20 μohm^{-1} m^{-1}, meaning that they were all neutral and nonionic. Similar results have been reported[14].

Table 1: Physical and analytical data for the ligands

Compd.	Molecular formular	Mol. Weight	Colour	Melting point (°C)	Yield (%)	Percentage found (calculated)		
						C	H	N
HPMAP	$C_{12}H_{22}O_2N_2$	216.03	White	58	60	65.42 (66.65)	5.77 (5.5)	12.60 (12.9)
HPMBP	$C_{17}H_{14}O_2N_2$	278.32	White	117	87	73.10 (73.36)	5.01 (5.0)	9.56 (10.07)
HPMBUP	$C_{14}H_{16}O_2N_2$	244.29	Yellowish Brown	85	85	68.68 (68.83)	6.78 (6.6)	11.30 (11.4)
HPMPRP	$C_{13}H_{14}O_2N_2$	230.27	Yellow	61	70	67.51 (67.81)	5.80 (6.1)	12.17 (12.1)
HPMCP	$C_{16}H_{20}O_2N_2$	272.35	Yellow	58	87	70.25 (70.56)	7.20 (7.4)	10.41 (10.2)
HPMPP	$C_{26}H_{40}O_2N_2$	412.55	Bone white	65	85	75.76 (75.70)	9.15 (9.7)	7.30 (6.76)

Table 2: Physical and analytical data for metal complexes

Compound	Molecular formular	Colour	Melting point (°C)	Yield %	Conductance $\mu ohm^{-1}m^{-1}$	Percentage found (calculated)		
						C	H	N
$Co(PMAP)_2.2H_2O$	$CoC_{24}H_{28}O_6N_4$	Pink	165	61	4.8	54.88 (54.69)	4.99 (4.87)	10.66 (10.62)
$Co(PMBP)_2.2H_2O$	$CoC_{34}H_{28}O_6N_4$	Pink	185	97	6.9	62.88 (62.79)	4.66 (4.61)	8.68 (8.63)
$Co(PMBUP)_2.2H_2O$	$CoC_{26}H_{34}O_6N_4$	Pink	146	89	7.2	57.4 (57.8)	5.7 (5.9)	9.7 (9.60
$Co(PMPrP)_2.2H_2O$	$CoC_{26}H_{30}O_6N_4$	Pink	159	98	13.5	56.2 (56.4)	5.7 (5.5)	9.4 (9.2)
$Co(PMCP)_2.2H_2O$	$CoC_{32}H_{44}O_6N_4$	Pink	138	72.69	2.7	42.76 (42.98)	2.39 (2.83)	2.68 (2.83)
$Co(PMPP)_2.2H_2O$	$CoC_{52}H_{82}O_6N_4$	Pink	99	99	15.1	68.2 (68)	9.15 (9.0)	6.0 (6.1)

Solubility data

The solubility data in Table 3 shows that all the complexes are hydrophobic which means that the distribution of these complexes from aqueous media into the organic media such as dioxane, acetone, benzene CCl_4 in which they are slightly soluble is favourable. The complexes all showed high degree of solubility in DMSO and DMF. These two solvents have lone pairs of electron, which they must have donated to the complex to complete the octahedron in the complex, thereby reducing further the ionic character of the complex, thus an increase in solubility of the complex in the two solvents. Similar observations has been reported previously[16,17].

Table 3: Solubility data for the Cobalt (II) complexes in various solvents

Solvents	Co-PMAP	Co-PMBP	Co-PMBUP	Co-PMCP	Co-PMPRP	Co-PMPP
Water	I	I	I	I	I	I
Methanol	SP	SP	I	I	I	I
Ethanol	SP	SP	I	I	SP	I
D.Ether	SP	VS	SP	S	SP	VS
Acetone	SP	SP	SP	I	SP	SP
Dioxane	SP	S	S	S	S	S
THF	VS	VS	VS	VS	SP	VS
CCL_4	SP	VS	VS	VS	SP	VS
n-Hexane	I	S	S	SP	S	SP
Pyridine	VS	VS	VS	S	VS	VS
Benzene	I	S	S	SP	SP	SP
DMF	VS	VS	VS	VS	VS	VS
DMSO	VS	S	S	VS	VS	VS

Legend: VS=very soluble, S=soluble, SP=sparingly soluble, I= insoluble

Electronic spectra

The electronic spectra of the the ligands and complexes are shown in Table 4. The complexes showed absorption bands between 298 nm and 364 nm in the ultraviolet region due to intraligand-transitions. Similar bands have been reported[14,16,17] for other metal chelates of the 4-acyl-pyrazolone-5 ligand. This observation suggests the possibility of the bonding system in the free ligand being preserved in the metal complex. No d-d transitions were observed and this may be due to the weakness of the bands or were obscured in the intense-bands.

Table 4: Electronic spectral data of the Cobalt (II) complexes of some 4-acyl pyrazol-5-one

Complex (Ligand)	$\lambda_{1\ max}$ (nm)	E_1	$\lambda_{2\ max}$ (nm)	E_2
CoPMAP (HPMAP)	317 (329)	1.4×10^{-3}	364.2 (359.4)	1.0×10^{4}
Co-PMBP (HPMBP)	303.6 (321.8)	1.1×10^{4}	356.8 (354)	2.1×10^{3}
CoPMBUP (HPMBUP)	296 (328.2)	5.6×10^{3}	361.2 (360)	2.6×10^{4}
Co-PMCP (HPMCP)	298 (322.6)	6.9×10^{3}	368.2 (334)	1.7×10^{3}
CoPMPRP (HPMPRP)	314 (327.4)	1.43×10^{4}	343.6 (360)	3.6×10^{4}
Co-PMPP (HPMPP)	293.4 (321.8)	3.2×10^{3}	364.2 (326)	9.0×10^{3}

Infrared spectral evidence

The infrared spectral data for ligands and complexes are shown in Table 5 and 6, respectively. The broad absorption band centred at 3400 cm^{-1} in the IR spectra of the metal complexes as shown in Table 6 have been assigned to adduct water molecule coordinated to the central metal ion and residing in the crystal lattice of the complex. The intense broad band centred at 2600 cm^{-1} in the IR spectra of the enol form of the ligand (Table 5) was observed to have disappeared in the spectra of the metal complex, indicating the involvement of the hydroxyl (-OH) in bonding resulting in the formation of a metal oxygen bond (M-O) in place of the hydrogen-oxygen bond (H-O) in the ligand anion. Similar results have been reported by previous researchers[14,16].

The appearance of the infrared carbonyl stretching bands (√C=O) of the metal chelates at higher frequencies when compared with that of the ligands suggests that the carbonyl group was involved in the bonding, resulting in the formation of a C=O-Co bonding system. It was also observed that there was a slight change in the stability of C=O-Co bonding system as the nature of the 4-acyl substituent changed. There was an observed increase in the carbonyl stretching bands of the metal chelates as the number of carbon atoms of the alkyl substituent increased, thus leading to an increase in the stability of the C=O-Co bond. This has been attributed to increase in electron density around the C=O-Co bond as the length of the carbon chain increased. This observation is contrary to the reports of Uzoukwu and others[14], which concluded that the nature of the 4-acyl substituent has no effect on the stability of the C=C and C=O bonding system. Replacement of the alkyl group at the 4-acyl position with a benzoyl group led to a decrease in the carbonyl stretching frequency and thus a decreased stability of the C=O-Co bonding system. This observation was attributed to electronic and steric interactions between the benzoyl group and the pyrazolone moiety. Similar results have been reported by Okafor[18,19] and Okpareke[20].

Table 5: Infrared spectra of the ligands

HPMAP	HPMBP	HPMBUP	HPMCP	HPMPRP	HPMPP	Assigments
3468br	3467br	3470br	3467br	3469br	-	√-O –H-O of water
3065w	-	3065w	-	-	-	Aryl C-H
-	2581br	-	-	-	2677br	√-OH enol
1639vs	1646s	1617s	1634vs	1626s	1627s	√C=O
1592s	1597w	1562s	1595w	1572m	1594w	Phenyl ring √C=C
-	1572w	1562s	1562m	1527m	1558w	Pyrazole ring stretch
1500m	1497w	1499sh	1516vs	1504sh	1500w	√asC=C=C
1363w	1345s	1392s	1363w	1374w	1342s	√s C=O
1085vs	1107vs	1095m	1099m	1084w	1090s	C-H in plane deformation
1011w	992m	1001s	1005s	1003s	1004s	CH_3 Rocking
690vs	687s	691vs	691vs	689s	688vs	Chelate ring deformation
653m	-	642m	634vs	639vs	640w	Chelate ring deformation
580m	610vs	607m	607s	605m	607s	Chelate ring vibration
507s	534s	500s	507s	507s	547s	Chelate ring vibration

Legend = br = Broad, vs = very strong, S = strong, Sh sharp, W = weak, Vw = very weak, ν = Sretching frequency, β = bending or defomation, ν_{as} = Asymetric stretching, ν_s = Symetric stretching

Table 6: Infrared spectra of the Cobalt (II) complexes

Co-PMAP	Co-PMBP	Co-PMBUP	Co-PMCP	Co-PMPRP	Co-PMPP	Assignments
3341br	3401br	3401br	3392br	3421br	3401br	√-O-HO water
2985w	-	3060br	3092br	3061w	-	Aryl C-H
1623vs	1604s	1626vs	1641vs	1624vs	1646s	√as C=O
1594vs	1559m	1597sh	1595m	1597s	1595s	Phenyl ring C=C

Cont…

Co-PMAP	Co-PMBP	Co-PMBUP	Co-PMCP	Co-PMPRP	Co-PMPP	Assignments
1535s	-	1580s	1578s	1544w	1559s	Pyrazol ring stretch
1485vs	1499s	1509vs	1506vs	1509vs	1501sh	√as C=C=C
1375vs	1378m	1395s	1362s	1371w	1394m	√s C=O
-	1353m	1324m	1324s	1325w	1316w	βs CH_3
1080vs	1070w	1079w	1078vs	1079vs	1079vs	C-H deformation
1014m	1008w	1002w	1012s	1006vs	1001m	CH_3 Rocking
659s	690s	690vs	689vs	688s	689s	Chelate ring deformation
609s	-	665m	663w	662m	640w	Chelate ring deformation
609s	539s	614s	614s	-	607w	Chelate ring vibration
510s	539s	510vs	509vs	507s	507s	Chelate ring vibration
448s	447s	489vs	457vs	448s	466s	√M-O

Legend = br = Broad, vs = very strong, S = strong, Sh sharp, W = weak Vw = very weak v = Sretching frequency, β = bending or defomation, ν_{as} = Asymetric stretching, ν_s = Symetric stretching

The infrared frequency bands observed below 700 cm^{-1} are due to chelate ring and metal oxygen vibrations. The absorption bands between 447 cm^{-1} and 489 cm^{-1} (Table 4) has been assigned to vibrations of the metal oxygen bond √Co-O.[15]

CONCLUSION

A combination of conductivity, U.V and I.R measurements show that all the complexes formed were neutral bischelates coordinating through the depronated hydroxyl group of enol tautomer of the ligand and the carbonyl oxygen of the keto form. The electronic spectral data also showed that the bonding system of the ligand anion remained intact in the metal complex on chelation. Infrared spectral evidence showed that the stability of the C=C and C=O bonding system was affected by the nature of substituent at the 4-acyl position.

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REFERENCES

1. B. A. Uzoukwu and P. Oforji, 1-phenyl-3-methyl-4-triflouroacetyl-pyrazolone-5 as an Extraction and Spectrophotometric Reagent for Vanadium, J. Natur. Sci. Comm. Srilanka, **21(1)**, 103-109 (1993).
2. Y. Akama, K. Sata, M. Ukaji, T. Kawata and M. Kajitani, Studies on Extraction of Copper (II) with I-phenyl-3-methyl-4-acyl Pyrazolone-5, Polyhedron, **4(1)**, (1985) pp. 59-63.
3. S. J. Lyle and A. U. Witts, Inorg. Chem. Acta, **5**, (1985) p. 481.
4. H. Samuelson and A. Lempicki, J. Chemical Physics, **39**, (1963) p. 110.
5. C. C. Hinckley, Journal of American Chemical Society, **91**, pp. 5160-5169.
6. S. M. Hassany and I. H. Qureshi, Extraction of Group IB, IIB, III –VA Elements with i-phenyl-3-methyl-4-acyl Triflouroacetyl Pyrazolone-5, Journal of Radio analytical Chemistry, **40**, (1977) pp. 23-39.
7. B. A. Uzoukwu and K. Gloe, Seperation of U(VI) from V(V), Extraction and Spectrophotometric Analysis of V(V) with 1-phenyl-3-methyl Pyrazolone-5, Radiochemical Acta, **81**, (1998) pp. 33-37.
8. M. Y. Mirza and F. I. Nwabue, Studies on Extraction of Ti(IV), Ce(IV) and U(VI) with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one from Different Mineral Acids, Separation of Thorium, Titanium, Uranium and Rare Earths Radiochimica Acta, **27**, 47-50 (1980).
9. M. O. C. Ogwuegbu and K. K. Maseka, Studies on the Coordination Complexes of Calcium(II), Cadmium(II) and Tin (IV) with Nitro-benzoyl-5-oxo Pyrazol, Bull. Chem. Soc. Ethiopia, **12(1)**, (1998) pp. 27-33.
10. N. Burham, N. Abdel- Azeons and M. F. Manda-Elshahat, Removal of Pb and Cd from Aqueous Media and Fish Liver using Novel Polyurethane Foam Functionalized with Pyrazolone as a New Metal Ion Collector, Central Europian Journal of Chemistry, **7(3)** (2009) pp. 576-585.
11. W. Wagnat and A. L. Nadia, Synthesis of Novel Pyrazole, Coumarin and Pyridazine Derivatives Evaluated as Potential Antimicrobial and Antifungal Agents, J. Chilean Chem. Soc., **52(2)** (2007) pp. 1145-1149.

12. I. E. Talat, Synthesis and Biological Activity of Some New Pyrazoles (3-4-b) Pyrazines, J. Chinese Chem. Soc., **53** (2006) pp. 391-401.
13. S. Umetani and H. Frieser, Mixed Ligand Chelate Extraction of Lanthanides with 1-phenyl-3-methyl-4- Triflouroacetyl Pyrazol-5-one and Some Phosphorous Oxide Compounds, Inorganic Chemist, **26** (1987) pp. 3179-3181.
14. B. A. Uzoukwu, Synthesis and Characterisation of Cobalt (II) Complexes with Some 4-acyl Derivatives of I-phenyl-methyl-4-acyl Pyrazolne-5, Synth. React. Inorg. Met-Org. Chem., **23**, 1087-1095 (1993).
15. B. A. Uzoukwu, Spectroscopic Study of Manganese (II) and Zinc (II) Complexes of I-phenyl-3-methyl-4-acyl Pyrazolne-5 Specrochimica Acta, **49A(2)**, 281-282 (1993).
16. E. C. Okafor, The Metal Complexes of Heterocyclic β-diketones and their Derivatives VII. The Synthesis, Structure and I.R Spectral Studies of 1-phenyl-3-methyl-4-Triflouroacetyl Pyrazolone-5 (HPMTFP) and its Divalent Metal Complexes Spectrochimica Acta, **37A(11)** (1981) pp. 951-955.
17. E. C. Okafor, ^{1}H and ^{13}C NMR Spectral Studies of Some 1-phenyl3-methyl 4-acyl-Pyrazol-5-ones in Chloroform Spectrochimica Acta, **40(5)**, 397-401 (1984).
18. E. C. Okafor, The Synthesis, Structure and I.R Spectral Studies of Metal (II) Pyrazolone-5-one, Spectrochimica Acta, **37A (11)**, (1981) pp. 939-944.
19. E. C. Okafor, Observations on 1-phenyl-3-methyl-4-triflouro Acetyl Pyrazolone-5, A Promising Extracting Agent Talanta, **29(4)**, 275-278 (1982).
20. O. C. Okpareke, J. N. Asegbeloyin and E. C. Okafor, Synthesis and Spectroscopic Characterization Copper (II) Complexes of Some 1-phenyl-3-methyl-4-acyl Pyrazol-5-ones, Proceedings of the 33rd Annual International Conference of the Chemical Society of Nigeria, Abeokuta Nigeria, **1**, (2010) pp. 293-298.

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