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Synthesis and Spectroscopic Studies of 4-butanoyl-3-methyl-1-phenylpyrazol-5-one and its Manganese (II), Lanthanum (III), Zirconium (III), Vanadium (V) and Tungsten (VI) Complexes

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Abstract: ***This study is aimed at the preparation of 4-butanoyl-3-methyl-1-phenylpyrazol-5-one (HBPy) by the acylation of 3-methyl-1-phenylpyrazol-5-one with butanoyl chloride; and the metal complexes of the HBPy with Mn (II), La (III), Zr (III), V (V) and W (VI) ions. Characterization was done by elemental analysis, UV-visible, IR and conductivity measurements. Physical properties such as colour, melting points and solubility profile were also determined for both the ligand and the complexes prepared. The results show that the ligand and the metal ions formed neutral complexes of the general formula, $M(BPy)_n.X$ (where M = metal ion, BPy = the ligand anion; X = an adduct and n = number of ligand molecules that complexed to M); in which Mn (II) formed dihydrate bischelate, $Mn(BPy)_2.2H_2O$; V(V) formed a dioxo adduct bischelate of the type, $VO_2(BPy).HBPy$; W(VI) forms the dioxoaquo-bischelate, $WO_2(BPy)_2.H_2O$; while La (III) and Zr (III) formed dihydrated trischelate, $La(BPy)_3.2H_2O$ and $Zr(BPy)_3.2H_2O$ respectively. The ligand complexed through its keto oxygen and/ or the deprotonation of the enolic hydrogen in its keto-enol tautomer. The CO-M bond stretching frequencies of the metal complexes were compared and the result showed that, in general, the bond increases with a decrease in the reduced masses of the oxygen and metal ions bonded. The ligand and its metal complexes studied are not ionic in nature. The complexes, $Mn(BPy)_2.2H_2O$; $La(BPy)_3.2H_2O$ and $Zr(BPy)_3.2H_2O$ have been assigned octahedral while $VO_2(BPy).HBPy$ and $WO_2(BPy)_2.H_2O$ have pentagonal bipyramidal geometries. The solubility data show that the complexes are soluble in many of the organic solvents having lone pair of electrons; hence, these solvents can be used with other inert organic solvents such as chloroform (CH_3Cl) and carbon tetrachloride (CCl_4) as solvent mixtures for extraction of the metal ions from their aqueous solutions.***

Keywords: 4-butanoyl-3-methyl-1-phenylpyrazol-5-one, Synthesis, Metal ions, Complexes, Spectroscopic studies.

1. Introduction

Many reactions involved in processing minerals in aqueous solution lead to metal complex formation. Formation of coordination complexes in hydrometallurgical processes has been very common among processes such as leaching, solvent extraction, ion exchange, flotation and electroplating. It has been suggested that in electroplating, electrolyte baths having complex ions in solution provide the most effective and efficient plating characteristics and good quality deposits of uniform thickness. In some operations, such as solvent extraction and ion exchange, complex formation is just a pre-requisite (Ogwuegbu & Chileshe, 2000). In most of these processes, complex formation has been found to improve reaction kinetics and metal recovery (El-Sonbati et al., 2002).

In this respect, acylpyrazolone ligands have been used to advantage as metal extractants or chelating reagents in the spectroscopic determination of metals in traces (Zolotov & Kuzmin, 1977); and a great number of studies have appeared in the literature on their ability to complex formation with metals. Such reactions are broadly used in analytical chemistry for determination and isolation of almost all metal ions, due to quite a number of valuable properties of these complexes such as high extracting ability, intense colour of the complex extracts and low solubility of the complexes in some solvents (Ogwuegbu & Oforka, 1994). Moreover, the formation of the metal complexes with acylpyrazolones has been applied for the separation of elements with similar properties, i.e. lanthanides, coinage metals, actinides, early transition metals, etc (Nishihama, Hirai & Komasawa, 2001). 4-acylpyrazol-5-ones, as modified β-diketones, are able to extract metal ions at lower pH values than open-chain β–diketones (Mickler, Reich & Uhlemann, 1995). Therefore, they offer the possibility of avoiding the pH region where hydrolysis of the metal ions takes place.

Zolotov and Mizra also reported that acylpyrazolones can extract metal ions from more acidic solutions than other chelating agents. (Zolotov, 1965; Mizra, 1969). The advantage of extraction in more acidic solutions is that competing hydrolytic reactions can be eliminated (Ogwuegbu, Oforka & Spiff, 1996). This permits the chelating agents to effectively overcome the influence of other complex-forming reactions in the aqueous phase.

Another great advantage of acylpyrazolones is that different acyl groups can be introduced into the materials in order to vary their electronic and steric features, since both the size and functionality of the acyl group influence this behaviour (Jensen, 1968). . Furthermore, these acylpyrazolones are a useful class of compounds for studying the effects of physical and chemical properties on extraction and chelating behaviour.

Kruse and Mellon have used pyridine pyrazolone reagent to determine colorimetrically the free ammonia in water samples. (Kruse & Mellon, 1952).

The potential applications of pyrazolones in medicine as strong analgesic, antihistaminic, antipyretic, antibacterial and anti-fungal have been reported (Raman, Raja, Joseph and Ohaveeth, 2007; Sarbani, Jyoti and Nalla, 2008). Medicinal chemists have used pyrazolones extensively as scaffolds from which to design novel therapeutic agents (Brugel et al., 2006).

Selective extraction is a key step in many hydrometallurgical processes. Amongst the many reagents which have been examined as extractants, the 1-phenyl-3-methyl-4-acylpyrazoral–5–ones; $RCOC_{10}H_8N_2OH$, have several advantages, which include strong acidity of the ligands, high stability and hydrophobicity of their chelates. They are more efficient extractants for metal ions in strong acid solutions and are cheaper than the widely used 4,4,4-trifluoro-1-(2-thienyl) -1,3-butanedione (Rao et al., 1977).

Obviously, the potential applications of 4-acylpyrazolones in medicine, in the extraction and construction of ion-exchange resins for metal ions are the incentive behind the investigation of the interaction between these chelating agents and metal ions in solution (Marchetti and Pettinari, 2005).

The structures of the keto–enol tautomeric forms of the 4-butanoyl-3-methyl-1-phenylpyrazol-5-one (designated here as **HBPy)** are as shown in figure 1 below.

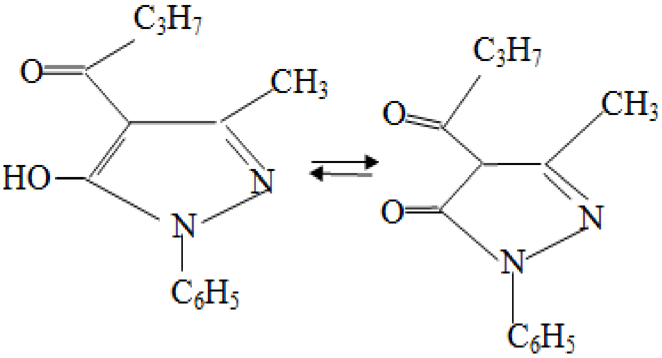

Figure 1: Structures of the keto-enol tautomeric forms of the 4-butanoyl-3-methyl-1-phenylpyrazol- 5-one.

The present study was carried out to synthesize and characterize the 4-butanoyl derivative of the 3-methyl-1-phenylpyrazol-5-one and its Mn (II), Zr (III), La (III), V (V) and W (VI) complexes; to understand the mode of interaction between the metals and the ligand in aqueous solution, hence propose the possible structures and geometries of the complexes.

2. Experimental

2.1 Reagents

Analytical grade reagents were used. These included ethylacetoacetate, phenylhydrazine, butanoyl chloride, 95% ethanol, and different salts of the metals; Mn (II), Zr (III), La (III), V (V) and W (VI) in their pure forms, etc. Distilled de-mineralized water was also used.

2.2 Synthesis of the ligand (HBPy)

The ligand, 1-phenyl-3-methyl-4-butanoyl pyrazol-5-one (HBPy), was synthesized according to the procedure outlined in the literature (Jensen, 1959; Okafor et al, 1990; Ogwuegbu & Maseka, 1998; Arinze, Daniel & Ogwuegbu, 2012). First, the 1-phenyl-3-methylpyrazol-5-one was prepared from condensation between the phenylhydrazine and ethyl acetoacetate (Brian, et al, 1989). 50 g (49 ml, 0.384 mol) of ethyl acetoacetate and 40 g (36.5 ml, 0.37 mol) of phenylhydrazine were mixed in an evaporating dish and heated on a water bath in a fume cupboard for 2 hours, stirring from time to time with a glass rod. Heavy syrup was formed and allowed to cool to an extent; then, 100 ml of ether was added and stirred vigorously. The syrup, which is insoluble in ether, solidified within 15 minutes. It was filtered and washed thoroughly with ether to remove coloured impurities and recrystallized from hot water. Colourless crystals were formed, with melting point of 127.3^{o}C.

15.0 g of the 1-phenyl-3-methylpyrazol-5-one were dissolved in 75 ml dioxane with gentle warming in a 500 ml three-necked round bottom, quick-fit flask equipped with a magnetic stirrer, separating funnel and reflux condenser. 12 g of calcium hydroxide were added to form a paste; followed by drop-wise addition of 10 ml butanoyl chloride within 2-5 minutes. The mixture was continuously stirred and gently refluxed for 90 minutes till the yellow calcium complex was formed. It was allowed to cool and the calcium complex decomposed by pouring in 200 ml of 2 M HCl, whereby cream coloured crude crystals precipitated and was recrystallized from an ethanol-water (65% – 35%) mixture slightly acidified to destroy any undecomposed calcium-complex. The product, 1-phenyl-3-methyl-4-butanoylpyrazol-5-one (HBPy) was identified through elemental analysis and spectroscopically (Uzoukwu, 1990).

It was then used in extracting the metal ions of interest: Mn (II), La (III), Zr (III), V (V) and W (VI), from their aqueous solutions, thereby forming their metal complexes.

2.3. Preparation of the Metal Complexes

The Mn (II), L,a (III), Zr (III), V (V) and W (VI) solutions were prepared by dissolving respectively: 0.50 g (0.025 M) $MnCl_2.4H_2O$, 0.82 g (0.025 M) $Na_2WO_4.2H_2O$, 0.3 g (0.025 M) NH_4VO_3, 0.55 g (0.017 M) $ZrOCl_2.8H_2O$ and 1.24 g (0.017 M) $La_3(SO_4)_2.9H_2O$ in 100 ml of water with warming.

Note: For the Na_2WO_4 and NH_4VO_3, the masses were dissolved in 2 ml 5 M HCl solution in order to generate only their WO_2^{2+} and $V0^+_2$ in the aqueous solution (Bieluonwu, 1995). Each solution was added drop wise with stirring to a hot 100 ml ethanol solution of 1.22 g (0.05 M) of the HBPy ligand (complexing agent). This gave a complex of metal-ligand mole ratio of 1:2 for Mn (II), V (V) and W (VI) and 1:3 for La (III) and Zr (III); as the complexes precipitated out gradually on cooling the solution. The crystalline product in each case was washed, recrystallized from aqueous ethanol (1:1), filtered, air–dried and stored over silica gel in a desiccator (Ogwuegbu, 1999).

3. Physical and Chemical Methods

The ligand and the complexes were subjected to IR, UV-visible, elemental or microanalytical analysis, conductivity, solubility in different solvents, melting points, and colour. The Infrared spectral measurements were obtained on a Shimadzu 8400 FTIR spectrophotometer. All samples were prepared as transparent KBr pellets using a tenton Carver press. UV-visible spectra were recorded on a Pye Unicam SP8-100 spectrophotometer. Conductance measurements were made with a Philips PW 9506 conductivity meter. The melting points were determined using the simple capillary tube method. Elemental analyses were also carried out while the solubilities of the ligand and the complexes were carried out in various solvents. The colours were recorded as observed (Uzoukwu, 1993).

4. Results and Discussion

The results of the analyses and their discussion are presented below.

4.1 Micro-analytical Data

The micro-analytical data are listed in Table 4.1. The elemental analysis data in table 4.1 shows that in aqueous solution, the mode of interactions between the metal ions and the ligand are in the mole ratios of 1:2 for Mn (II), V(V) and W (VI) and 1:3 for La (III) and Zr (III), and associated with molecules of water of crystallization from aqueous solution. The complexes conform to the general molecular formula $ML_n.XH_2O$, where n is the oxidation state of the metal, M or the number of the ligand, L is the anionic ligand (BPy^-), X is the number of water (H_2O) molecules in all but V (V); having the values of 1 for WO_2L_2 and 2 for Mn (II), La (III) and Zr (III); in V (V), X is HBPy.

4.2 Conductivity Measurements

The conductivity measurements on both the ligand and the metal complexes in acetone (10^{-3} M) gave values lower than 30 S mol^{-1} cm^{-1}, showing that they are non-ionic compounds (Uzoukwu & Adiukwu, 1996). No values were observed for the ligands, indicating their pure covalent nature. In all, the Mn (II) complex has the highest value of 15.1 S mol^{-1} cm^{-1} while tungsten (VI) and vanadium (V) have the lowest conductance values of 5.7 S mol^{-1} cm^{-1} and 6.8 S mol^{-1} cm^{-1} respectively. This could be as a result of the two oxo (O=M=O) groups in their coordination sphere which tend to decrease the electronegativity differences of the metal ions and the anionic ligands further, thus making the complexes more covalent than they could have been and reducing their formation of mobile ions, culminating into their lower conductance.

4.3 Melting Points

The melting point determination of the ligand and the complexes show that all the complexes have higher values than the ligand. This further confirms the more ionic nature of the former as was observed in their conductance values. Tungsten has the highest value of all the complexes. This is not unconnected to the metal itself which has a very high melting point of about 3300°C and is found use in making filaments in electric light bulbs (Lee, 2005).

Table 4.1: Physical and micro-analytical data for the ligand and the metal complexes:

Compound	Molecular formula	Colour	% Yield	Melting Point	Conductance S $mol^{-1}cm^{-1}$	% Found (Calculated) C	H	N
HBPy	$C_{14}H_{16}N_2O_2$	Yellowish-brown	85	87.2	-----	68.52 (68.85)	6.48 (6.56)	11.52 (11.48)
$Mn(BPy)_2.2H_2O$	$MnC_{28}H_{34}N_4O_6$	Pale- yellow	70	182	15.1	58.11 (58.23)	5.82 (5.89)	9.80 (9.71)
$La(BPy)_3.2H_20$	$LaC_{42}H_{49}N_6O_8$	Yellow	97	170	10.8	55.68 (55.75)	5.22 (5.42)	9.32 (9.29)
$Zr(BPy)_3.2H_2O$	$ZrC_{42}H_{49}N_6O_8$	Pink	61	208	11.7	58.62 (58.88)	5.90 (5.72)	9.72 (9.81)
$VO_2(BPy).$ HBPy	$VC_{28}H_{31}N_4O_6$	Whitish- yellow	62	245	6.8	58.84 (58.95)	5.20 (5.44)	9.81 (9.82)
$WO_2(BPy)_2.H_2O$	$WC_{28}H_{32}N_4O_7$	Dirty-white	66	298	5.7	46.58 (46.67)	4.63 (4.44)	7.65 (7.78)

4.4 Solubility Data

The solubility data in Table 4.2 show that the ligand and all the complexes are hydrophobic which means that the distribution of these complexes from aqueous media into organic media such as acetone, ethylacetate, chloroform, tetrahydrofuran (THF), dioxane, benzene, etc in which they are slightly soluble is favourable. The complexes showed high degrees of solubility in ethylacetate, acetone, DMSO, THF, dioxane and pyridine. These solvents have lone pairs of electrons, which they must have donated to the complexes to complete the octahedron in the complexes, thereby reducing further the ionic character of the complexes, thus an increase in the solubility of the complexes in those solvents. In effect, these solvents can be used with other inert organic solvents such as chloroform (CH_3Cl) and carbon tetrachloride (CCl_4) as solvent mixtures for extraction of these metal ions from their aqueous solutions, especially for those metals that form hydrated complexes which do not have all the coordination sites saturated by the organic reagents. Similar observations have been reported previously (Okafor, 1984).

Table 4.2: Solubility data of the HBPy ligand and its metal complexes in various solvents:

Solvent	HBPy	$Mn(BPy)_2$	$La(BPy)_3$	$Zr(BPy)_3$	$VO_2(BPy)_2$	$WO_2(BPy)_2$
ethylacetate	vs	vs	vs	vs	vs	vs
chloroform	vs	ss	s	s	s	s
xylene	vs	is	ss	ss	ss	ss
petroleum ether	ss	ss	ss	ss	ss	ss
toluene	vs	is	s	s	is	ss
methanol	ss	is	ss	is	is	is
cyclohexane	is	is	is	is	is	is
n-hexane	is	is	is	is	is	is
cyclohexanol	vs	vs	vs	vs	vs	vs
propan-2-ol	ss	s	s	s	s	s
ethanol	ss	is	is	is	is	is
diethylether	vs	vs	s	s	s	s
acetone	vs	vs	vs	vs	s	s
dmso	vs	vs	vs	vs	vs	vs
dioxane	vs	vs	vs	vs	vs	vs
water	is	vs	is	is	is	is
acetonitrile	vs	vs	vs	vs	vs	vs
benzene	vs	ss	ss	ss	ss	ss
thf	vs	vs	vs	vs	vs	vs
pyridine	vs	vs	vs	vs	vs	vs

Legend: s = soluble, is = insoluble, ss = slightly soluble, vs = very soluble.

4.5 Electronic Spectra

The electronic spectral data of the ligand and the metal complexes are given in Table 4.3. The absorption maxima λ_1 and λ_2 occur in the spectra of both the ligand and the metal complexes, at between 326 nm and 368 nm in the near ultraviolet region. The ligand and the metal complexes have virtually identical spectra. This suggests that the π-bonding system in the ligand is almost intact in the ligand anion of the metal complexes (Okafor, 1991); indicating that there is no interaction between the metal ions and the π-bonding system of the ligand. Absorptions at this regions are therefore ascribed to $\pi \rightarrow \pi^*$ transitions. Therefore, the coordination (interaction) between the metal ions and the ligand is mainly through δ-bond formation between metal ions (M^{n+}) and the oxygen atoms of the carbonyl group (C=O) of the ligand. No d-d transitions were observed and this may be due to the weakness of the bands or were obscured by the more intense $\pi \rightarrow \pi^*$ bands. The higher molar absorptivities of the chelates and the observed bathochromic shifts of the M^{n+} complexes indicate chelate formation between M^{n+} ions and the BPy^- anion (Uzoukwu, Gloe & Adiukwu, 2000).

Table 4.3: Electronic spectral data of the ligand and the metal complexes.

Ligand/complexes	λ_1 max (nm)	ε_1(L.mol^{-1}cm^{-1})	λ_2 max (nm)	ε_2 (L.mol^{-1}cm^{-1})
HBPy	328	5.6×10^3	360	2.6×10^4
$Mn(BPy)_2.2H_2O$	333	1.1×10^4	363	2.1×10^4
$La(BPy)_3.2H_2O$	328	3.0×10^3	359	5.5×10^2
$Zr(BPy)_3.2H_2O$	326	1.5×10^4	362	1.3×10^4
$VO_2(BPy).HBPy$	336	3.3×10^3	365	1.0×10^4
$WO_2(BPy)_2.H_2O$	331	3.2×10^3	368	9.0×10^3

4.6. Infra-red Spectra

The infrared spectral data for the ligand and complexes are found in table 4.4. The observed IR frequencies have been assigned by comparison with those of previous reports on 4-acylpyrazolones-5 and their metal complexes. The IR absorption spectra have been divided arbitrarily into three main spectral regions: 4000 cm^{-1} –1800 cm^{-1}, 1800 cm^{-1} – 1000 cm^{-1} and 1000 cm^{-1} – 400 cm^{-1} for easier explanation and understanding.

(a) 4000 cm^{-1} –1800 cm^{-1} region: The strong and weak absorption peaks in the range 3483 – 3765 cm^{-1} observed in the ligand are attributed to νOH vibrations of the enol (Adeniyi et al, 2006). Similar broad bands centred between 3412 – 3761 cm^{-1} in the IR of the metal complexes have been assigned to the νOH of the adduct water molecules coordinated to the central metal ion and residing in the crystal lattice of the complexes. (Okpareke et al., 2012). The intense very strong peak at 3620 cm^{-1} of the ligand is assigned to the νO-H frequency of the enol form of the ligand was not observed in the spectra of the metal complexes, 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, i.e., deprotonation of the OH group of the ligand and its replacement by the metals during chelation.

(b) 1800 cm^{-1} – 1000 cm^{-1} region: The band spectra occurring at 1600 –1700 cm^{-1} region is due to carbonyl (C=O) and C=C frequencies of the chelate ring. Studies on β-diketones showed that νC=O occurs at a higher frequency than C=C. (Uzoukwu & Adiukwu, 1995). The νC=O stretching band of the ligand was observed as very strong peak at 1753 cm^{-1}, together with the V complex; but those of the other metal complexes except Mn, were below this value (1653 – 1745 cm^{-1}; Mn complex showed a very weak band at a higher value of 1884 cm^{-1}); indicating the involvement of the C=O group in the chelation process. It is pertinent to note that the shift in νC=O of Mn(BPy)$_2$ occur by 16 cm^{-1}, Zr(BPy)$_3$ by 8 cm^{-1} and WO$_2$(BPy)$_2$ by 56 cm^{-1}, indicating that C—O—Zr bond of the Zr(BPy)$_3$ complex is relatively weaker. The large bathochromic shift of about 56 cm^{-1} in WO$_2$(BPy)$_2$ complex indicates stronger M-O bonds; and not shifted in VO$_2$(BPy)$_2$ while it was not observed in Mn(BPy)$_2$. 1440 –1485 cm^{-1} absorption bands have been assigned to –CH$_3$ bending vibration; while the bands at 1230 – 1384 cm^{-1}are assigned to the carbonyl (C=O) and C=C symmetrical stretching frequencies of the chelate ring. These values are present both in the ligands and the complexes. The ligand and all the metal complexes showed strong absorption bands around 1120 – 1251 cm^{-1} region and this has been assigned to C-H vibrational frequency resulting from bending vibrations in the molecule. The vibrational frequency modes observed between 1103 and 1016 cm^{-1} have been assigned to C-H in-plane deformation of the phenyl ring in the complexes. The comparison of the spectra of the ligand with those of the metal complexes show that there is little or no shift in the above frequencies indicating that the π-system of the unsubstituted phenyl ring of the free ligand moiety is not involved in the coordination with the metal ions studied. **(c) 1000 –400 cm^{-1} region:** The vibrational frequency modes of interest in this region are those due to the chelate ring and metal-ligand vibrations. This region provides information on the effect of the 4-acyl substituent on the stability of the metal-oxygen bond. The presence of bands between 600 – 400 cm^{-1}, which are typical of 1,3-diketonates have been suggested as due to bonding to metals through the oxygen atom of the ligand. (Okafor, Adiukwu & Uzoukwu, 1993). The weak bands in the IR spectra of the metal complexes appearing at 422cm^{-1} for Mn(BPy)$_2$, 434 cm^{-1} for La(BPy)$_3$ and WO$_2$(BPy)$_2$, 464 cm^{-1} for VO$_2$(BPy)$_2$; and 435 cm^{-1} for Zr(BPy)$_3$ are absent in the ligand. These have been assigned to νM-O of the metal complexes. The trend of νM-O in the complexes follows the order: V > Zr > = La = W > Mn. This, in general, is in accordance with decrease in their reduced masses which follows the order: V < Mn < Zr < La < W (having reduced masses; O-M bonds, of 12.18, 12.39, 13.61, 14.35 and 14.72 respectively); since frequency of vibration is inversely proportional to reduced mass, expressed as: $V_o = 1/2\pi\sqrt{k/\mu}$; where V_o = frequency and μ = reduced mass (Kemp, 1975).

Table 4.4: The IR Spectral data for the HBPy ligand and its metal complexes and approximate assignments

HBPy	Mn(Bpy)$_2$	La(BPy)$_3$	Zr(BPy)$_3$	VO$_2$(BPy)$_2$	WO$_2$(BPy)$_2$	Assignments
3753w	3751w	3747w	3753m	3743m	3761m	νO-H of water
3620m	---------	---------	------------	----------	---------	νO-H of enol
--	3369b	3587w	3448b	3454b	3448b	νO-H of water
3063b	3061w	3412b	3061m	3068w	-------	Aryl C-H
2929w	2929w	2929w	2928m	2922s	2924m	νC-H
--------	---------	--------	2856w	2854m	2858w	
2374w	2372w	2364m	2366m	2374m	2364s	$_{\beta}$O-H of water
1953vw	1957vw	--------	1955w	-------	-------	$_{\beta}$O-H of water
1880vw	1884vw	--------	-------------	----------	--------	
1753s	-------	1737w	1745m	1753vs	-----	νC=O
-------	----------	1653s	------	1712m	-----	
1620vs	1612b	1643s	1606vs	1608s	1631s	ν_{as}C=O
-------	--------	------	1577w	1548s	------	Phenyl ring νC=C
-------	------------	-------	1523w	1506w	1525m	Pyrazole ring stretch
1491vs	1485b	1475m	1479s	-------	1473m	ν_{as}C=C=C
1440m	1435w	1442w	1431w	1446m	------	$_{\beta as}$CH$_3$
1353w	1361s	1357w	1384m	1384m	-----	ν_sC=O
--------	------	--------	-------	1301b	------	
1230s	1232m	-------	1251w	1236w	-------	ν_sC=C=C
1161b	1157m	1180s	1163s	1163m	1165w	C-H in plane deformation
--------	-------	-------	1120w	1103m	----	C-H deformation
1064m	1062m	1057s	1066s	1045m	-----	C-H deformation
1016vs	1022m	------	1020m	1045m	-----	CH$_3$ rocking
943vs	945m	983m	949m	943w	-----	C-Phenyl stretch
914w	916w	----	916w	-----	-----	
------	-----	-----	-----	904m	-----	ν_{as}O=M=O
839m	839m	837w	840m	839s	-----	γC-H
-----	-----	-----	------	-----	798b	ν_{as}O=M=0
761vs	761vs	746w	763vs	754s	-----	γC-H
698vs	698vs	-----	696vs	704m	-----	Chelate ring deformation
613m	613m	628vs	623s	621m	-----	Chelate ring deformation
542m	551m	-----	553m	553m	-----	Chelate ring vibration
507m	507s	509w	501b	507m	------	Chelate ring vibration
-----	442w	461w	-----	464m	-----	νM-O
-----	-----	434w	435m	434m	434w	νM-O

Legend: b = broad, m = medium; s = strong; vs = very strong; w = weak; vw = very weak; $^{\beta}$ = bending or deformation; ν = stretching frequency; ν_s = symmetric stretching; ν_{as} = Asymmetric stretching; γ = out of plane bending.

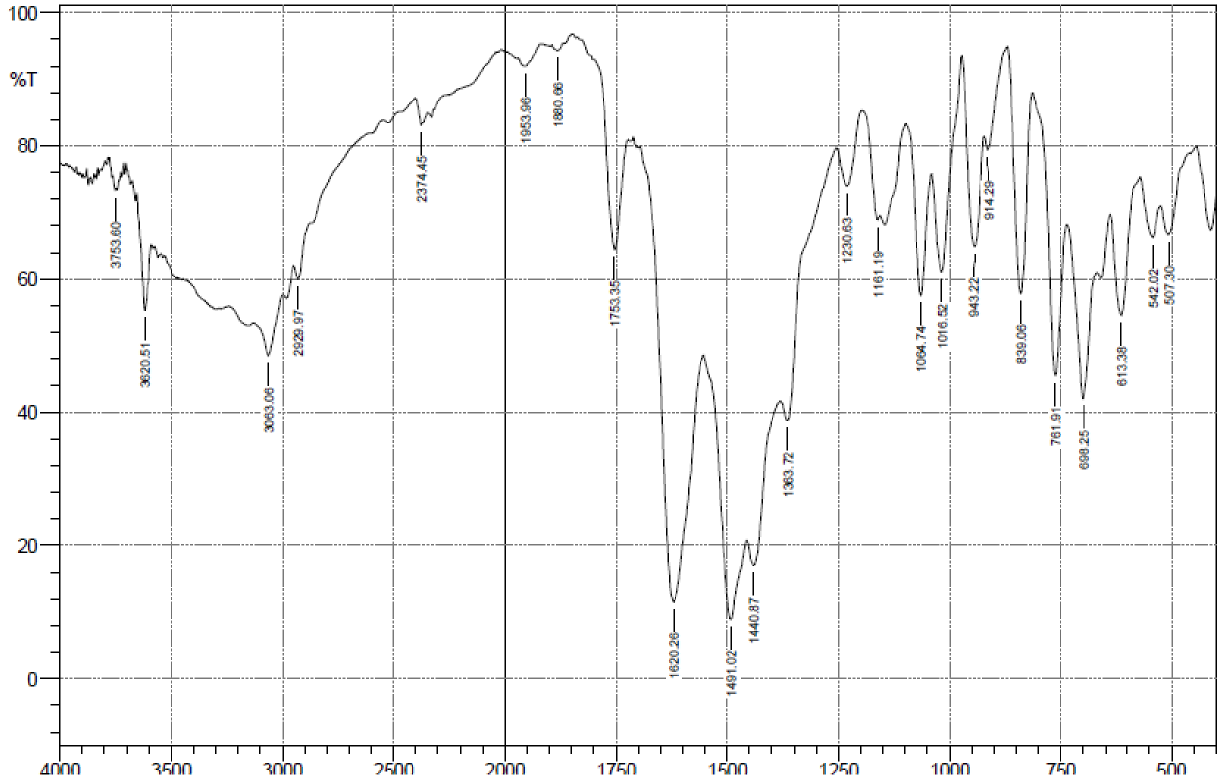

Figure 4.41: IR spectrum of 1-phenyl-3-methyl-4-butanoylpyrazol-5-one, (HBPy)

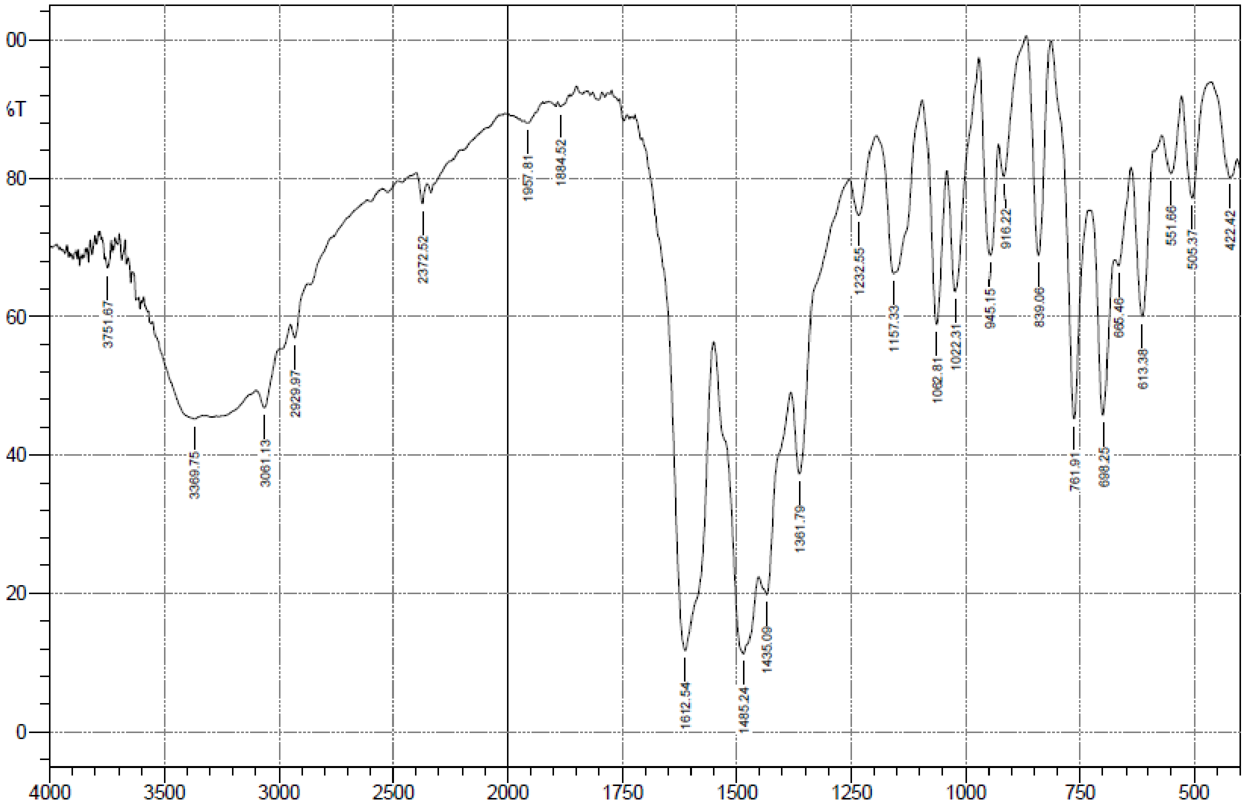

Figure 4.4.2: IR spectrum of $Mn(BPy)_2.2H_2O$

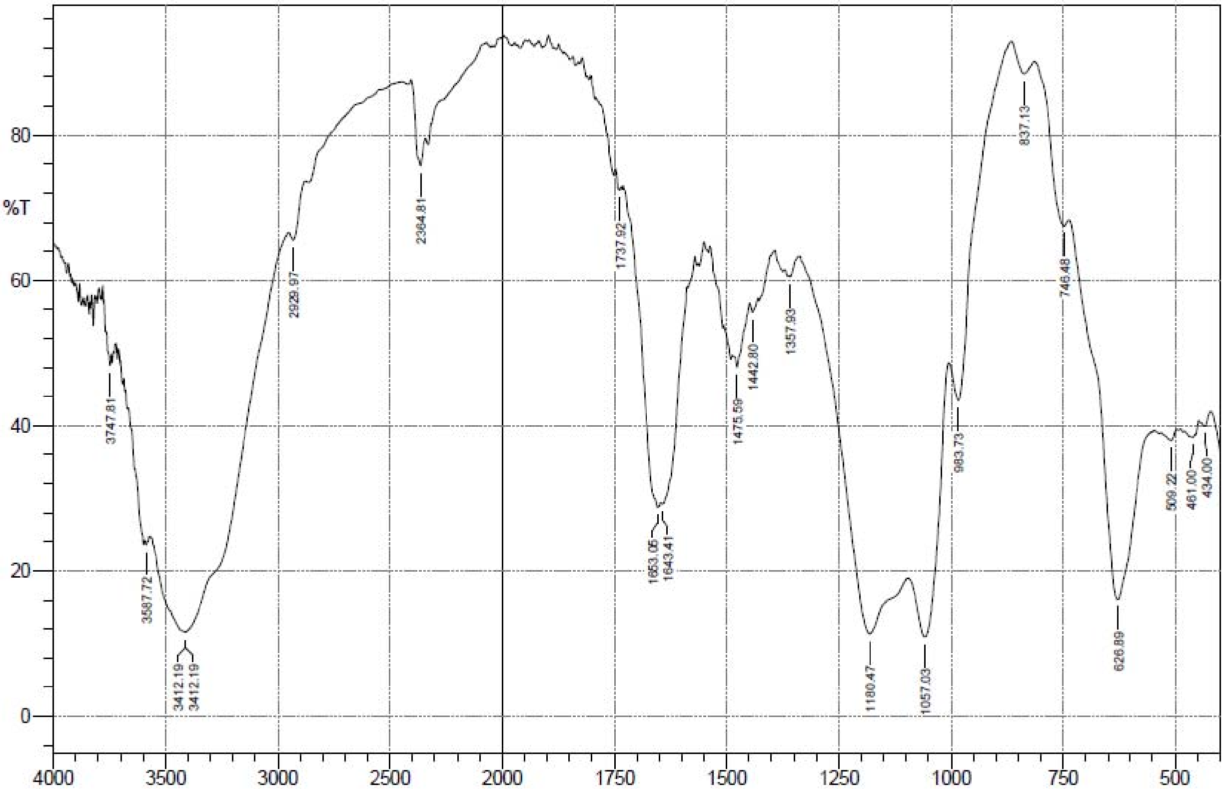

Figure 4.4.3: IR spectrum of La$(BPy)_3.2H_2O$

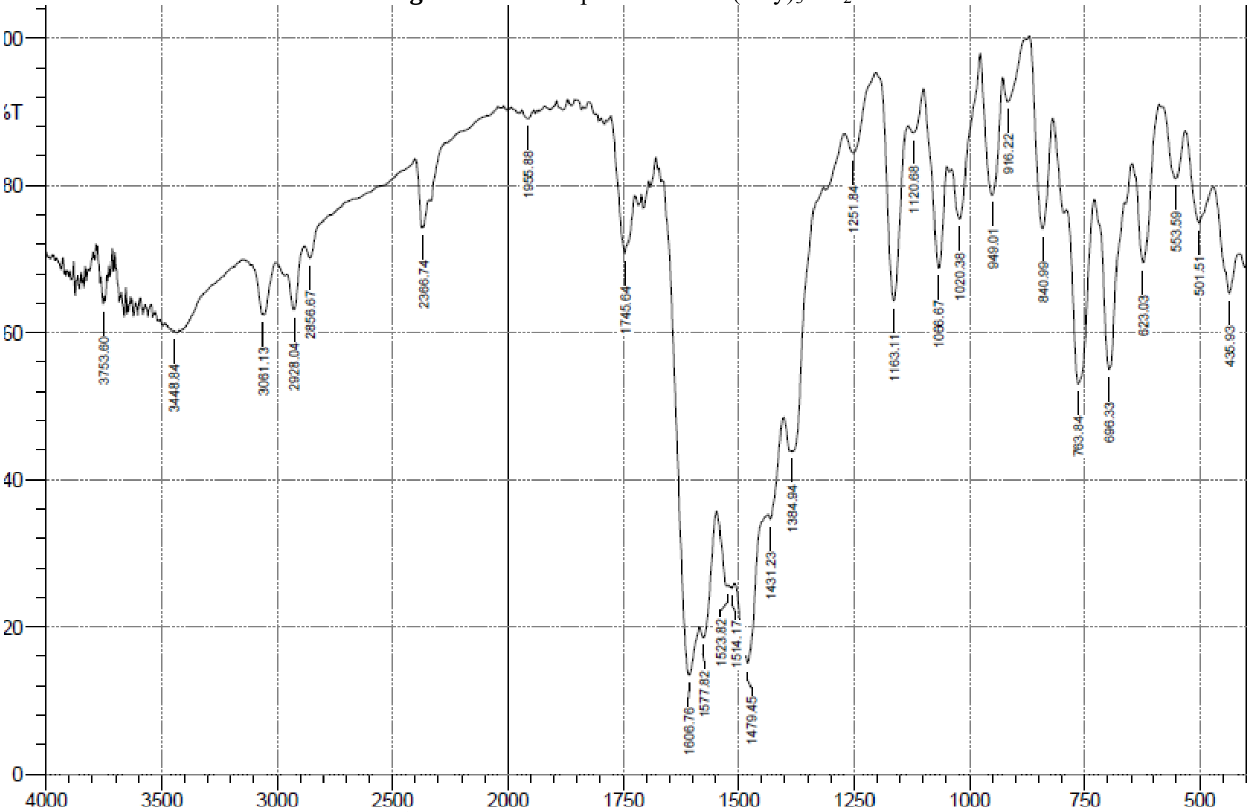

Figure 4.4.4: IR spectrum of Zr$(BPy)_3.2H_2O$

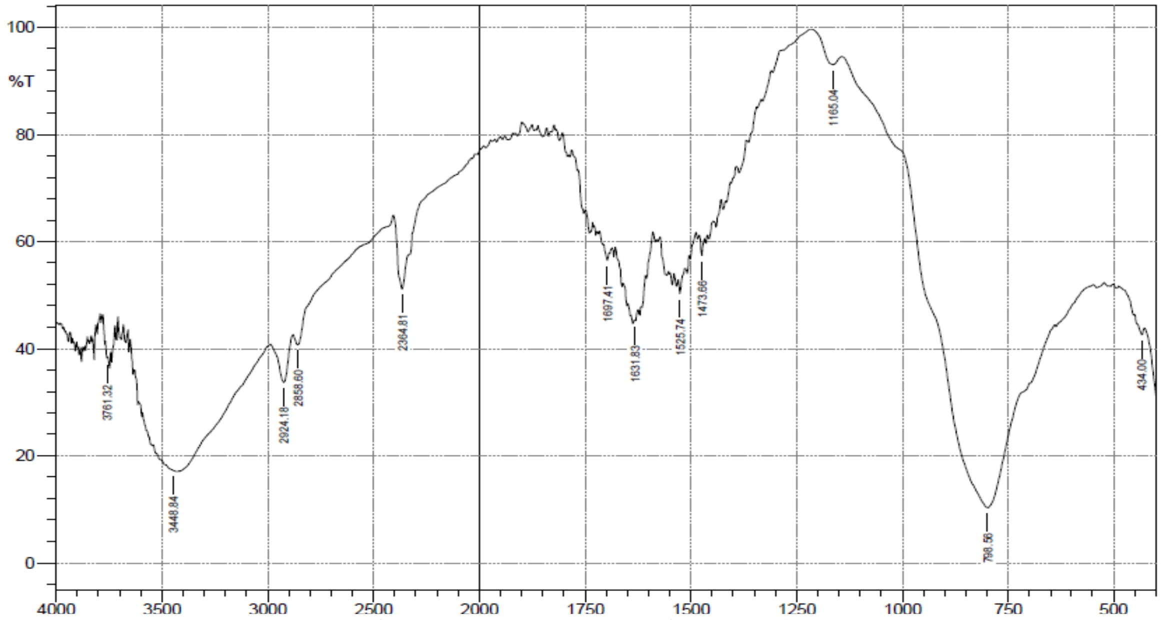

Figure 4.4.5: IR spectrum of $WO_2(BPy)_2.H_2O$

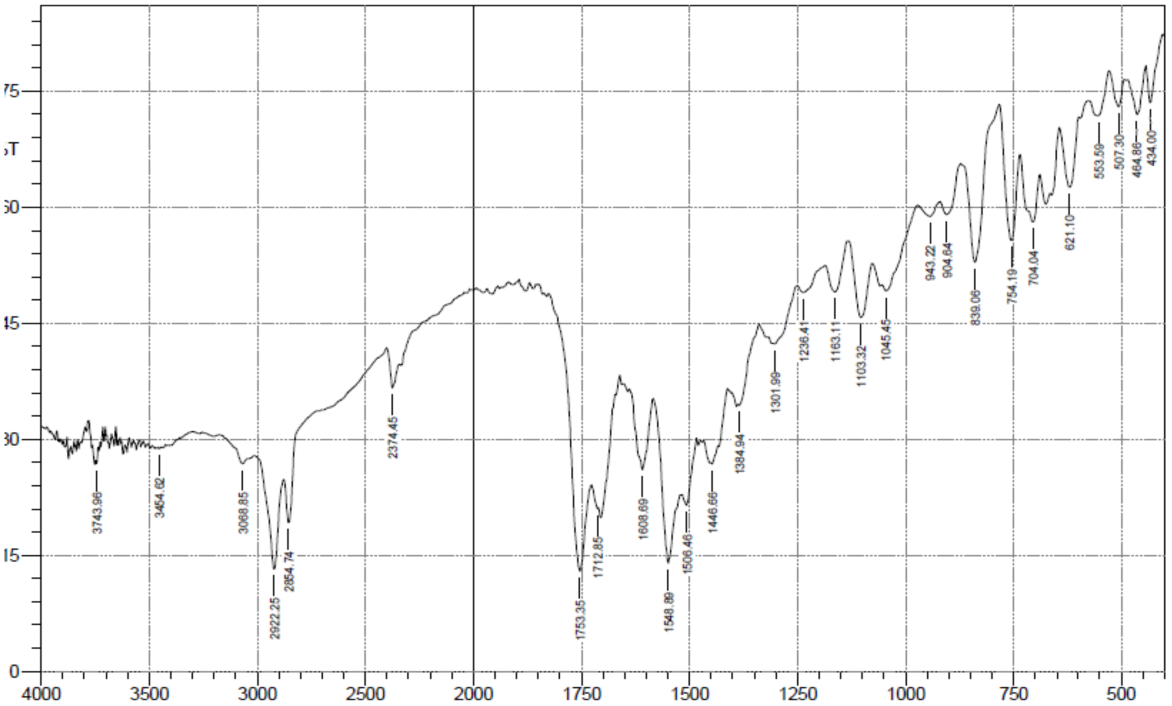

Figure 4.4.6: IR spectrum of $VO_2(BPy).HBPy$.

4.7 Conclusion

From the results of the analyses, the structures of the complexes are as shown below:

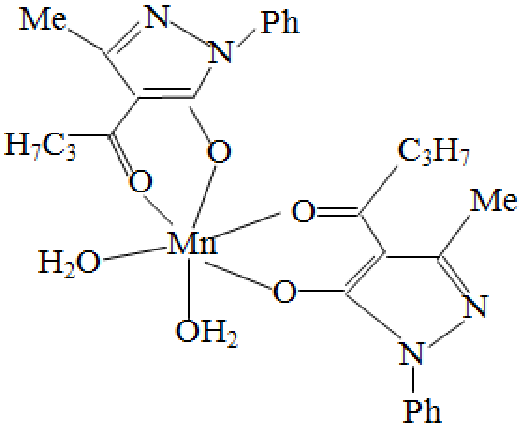

Figure 4.7.1: Structure of the manganese complex of the pyrazolone derivative, [Mn(BPy)$_2$.2H$_2$O]; Octahedral geometry; Ph = Phenyl (C$_6$H$_5$), Me = Methyl (CH$_3$).

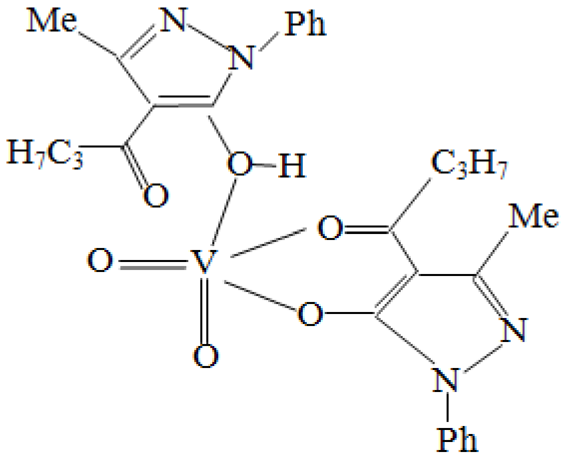

Figure 4.7.2:. Structure of the dioxovanadium (V) pyrazolonate derivatives, [VO$_2$(BPy).HBPy]; Pentagonal bipyramidal.

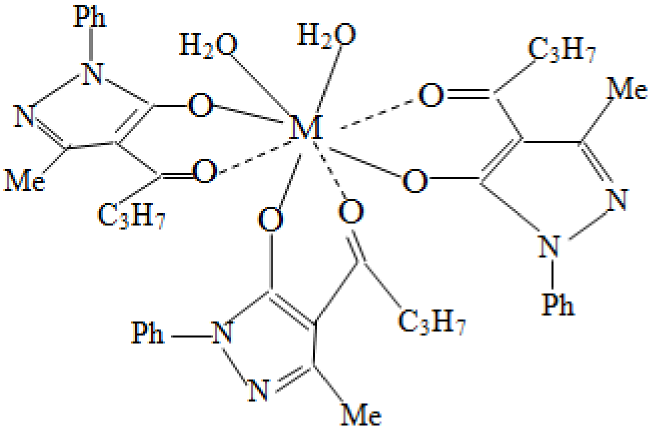

Figure 4.7.3: Structure of [La(BPy)$_3$.2H$_2$O)] or [Zr(BPy)$_3$.2H$_2$O)] ; Octahedral geometry; M = La or Zr.

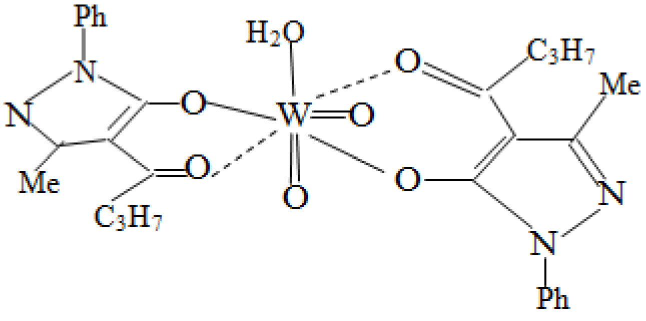

Figure 4.7.4: Structure of the tungsten-pyrazolone derivative, [WO$_2$(BPy)$_2$.H$_2$O]; Pentagonal bipyramidal.

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