



## Synthesis and Characterization of 1-phenyl-3-methyl-4-stearoylpyrazol-5-one and Its Lanthanum(III) and Tungsten(VI) Complexes

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### Authors' contributions

This work was carried out in collaboration among all authors. Author AICE wrote the protocol, managed the literature, performed the statistical analysis and wrote the first draft of the manuscript. Author CKE supervised the statistical analysis and made necessary inputs in the study. Author CA prepared the samples, carried out the experiment. Author MOCO designed and supervised the study. Author ENOE guided and contributed to the experiment, statistical analysis and read through the first draft of the manuscript. All authors read and approved the manuscript.

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### ABSTRACT

The ligand, 1-phenyl-3-methyl-4-stearoylpyrazol-5-one (HSPy), and its La(III) and W(VI) complexes were synthesized and characterized spectroscopically using elemental analysis, UV-visible, IR, <sup>1</sup>H and <sup>13</sup>C NMR. Physical properties such as colour, melting points, conductivity measurements and solubility profile were also investigated. La(III) and W(VI) reacted with the ligand in the metal-ligand mole ratios of 1:3 and 1:2 to form neutral complexes of diaquo-trischelate La(SP<sub>y</sub>)<sub>3</sub>.2H<sub>2</sub>O and dioxoaquo-bischelate, WO<sub>2</sub>(SP<sub>y</sub>)<sub>2</sub>.H<sub>2</sub>O respectively.

**Keywords:** 1-phenyl-3-methyl-4-stearoylpyrazol-5-one; synthesis; characterization; lanthanum(III); tungsten(VI); complexes.

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## 1. INTRODUCTION

Acylpyrazolones are an interesting class of  $\beta$ -diketones, containing a pyrazolone fused to a chelating arm ( $R_3-C=O$ ) as shown in Figure 1.

The potential applications of 4-acylpyrazolones in medicine, in the extraction and construction of ion-exchange resins for metal ions are the incentives behind the investigation of the interaction between these chelating agents and metal ions in solution [1]. 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 as well as to optimize metal extraction and selectivity since both the size and functionality of the acyl group influence this behaviour [2]. A wide range of  $R_3$ -substituted 1-phenyl-3-methyl-4-acylpyrazol-5-one (Figure 1;  $R_1 = -C_6H_5$ ,  $R_2 = -CH_3$ ) have been synthesized and used as potential extractants of metal ions from aqueous solutions [3].

The syntheses, isolation and characterization of large alkylated  $R_3$  substituents in Figure 1, such

as  $-C_{17}H_{35}$  have not been extensively reported in the literature. This could be the reason why a number of applications of metal 4-acylpyrazolones, especially in medicine, NMR shift reagents and LASER materials have not received considerable attention [4].

In our earlier work [5], the 4-butanoyl ( $-C_3H_7C=O$ ) substituent and its complexes with some transition metals were studied. In the recent work, the  $R_3$  substituent has been extended to include  $-C_{17}H_{35}$ , hence the 4-stearoyl ( $-C_{17}H_{35}C=O$ ), a more alkylated homologue.

The structures of the keto–enol tautomeric forms of HSPy are shown in Figure 2.

The present study was carried out to synthesize and characterize the large alkylated  $R_3$  substituent ( $R_3 = -C_{17}H_{35}$ ) of the 1-phenyl-3-methylpyrazol-5-one and its La(III) and W(VI) complexes to access the mode of interaction between the metals and the ligand in aqueous solution and the possible structures of the complexes are proposed, relative to the 4-butanoyl ( $R_3 = -C_3H_7$ ) homologue [5].

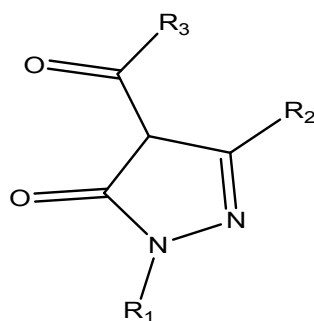


Figure 1. Generic structure for acylpyrazolones

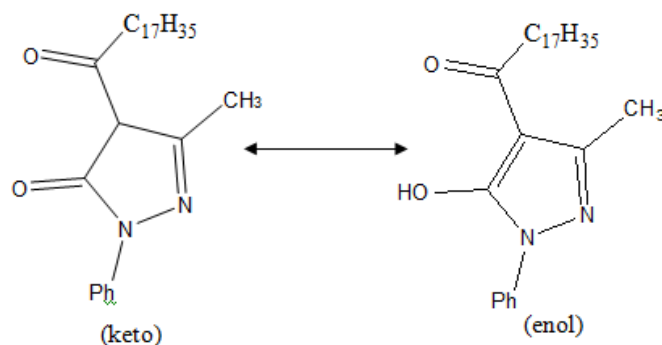


Figure 2. Structures of the keto-enol tautomeric forms of HSPy

## 2. EXPERIMENTAL AND METHODS

### 2.1 Reagents

Analytical grade reagents including ethylacetoacetate ( $\text{CH}_3\text{-C=OCH}_2\text{-COOCH}_2\text{CH}_3$ ), phenylhydrazine ( $\text{C}_6\text{H}_5\text{NH-NH}_2$ ), stearoyl chloride ( $\text{C}_{17}\text{H}_{35}\text{COCl}$ ), prepared according to the procedure outlined in the literature [5,6]. 95 % ethanol, distilled demineralized water,  $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  were in their pure forms, as purchased.

### 2.2 Synthesis of the HSPy

The 1-phenyl-3-methyl-4-stearoylpyrazol-5-one, designated as HSPy, is presented in Figure 2. It is the neutral form, considered as complexing agent. The ligand is the SPy form, in the complexes  $\text{La}(\text{SPy})_3 \cdot 2\text{H}_2\text{O}$  and  $\text{WO}_2(\text{SPy})_2 \cdot \text{H}_2\text{O}$ . It was synthesized according to the procedure outlined in the literature [5,7,8].

First, 1-phenyl-3-methylpyrazol-5-one was prepared from condensation between the phenylhydrazine and ethylacetoacetate. Then a 15.0 g portion of the 1-phenyl-3-methylpyrazol-5-one was 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. A 12.0 g of calcium hydroxide was added to form a paste followed by dropwise addition of 10 ml stearoyl chloride within 2-5 minutes. The mixture was continuously stirred and gently refluxed for 90 min till the yellow calcium complex was formed. It was allowed to cool and the calcium complex was decomposed by pouring in 200 ml of 2 M HCl, whereby cream coloured crude crystals precipitated and were recrystallized from an ethanol-water (65% – 35%) mixture slightly acidified to destroy any undecomposed calcium-complex. The product, 1-phenyl-3-methyl-4-stearoylpyrazol-5-one (HSPy) was identified through elemental analysis and spectroscopically [9].

### 2.3 Preparation of the Metal Complexes

The La(III) and W(VI) solutions were prepared by dissolving respectively: 1.24 g (0.017 M)  $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  and 0.82 g (0.025 M)  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  in 100 ml of water with warming.

**NOTE:** The  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  was dissolved in 2 ml 5 M HCl solution first, in order to generate the  $\text{WO}_2^{2+}$  before subsequent dilution to obtain the aqueous solution [10].

Each solution was added dropwise with stirring a hot 100 ml ethanol solution of 2.20 g (0.05 M) of the HSPy (complexing agent). The  $\text{La}(\text{SPy})_3 \cdot 2\text{H}_2\text{O}$  and  $\text{WO}_2(\text{SPy})_2 \cdot \text{H}_2\text{O}$  complexes precipitated out gradually upon cooling. The crystalline product was washed, recrystallized from aqueous ethanol (1:1), filtered, air-dried and stored over silica gel in a desiccator [11,12].

### 2.4 Physicochemical Measurements

The melting points of the ligand and the complexes were determined using the simple capillary tube method. The colours were recorded as observed [5,8]. Elemental analyses were carried out using a 2400 Series II- Perkin Elmer Carbon, Hydrogen, Nitrogen, and Oxygen Rapid Analyser. Conductance measurements were made with a Philips PW 9506 conductivity meter, which was standardized using 0.01 M KCl and the cell with platinum electrodes.

The solubilities of the ligand and the complexes were carried out in various solvents including water, ethanol, acetone, petroleum ether, n-hexane, etc.

### 2.5 UV-visible Characterization

UV-visible spectra were recorded on a 2500 PC spectrophotometer.

### 2.6 IR Characterization

The infrared (IR) spectral measurements of the ligand and the complexes were obtained in the  $4000\text{-}400\text{ cm}^{-1}$  on a Shimadzu 8400 FTIR spectrophotometer.

### 2.7 NMR Characterization

The proton and carbon-13 NMR spectral data in dimethylsulphoxide (DMSO) were obtained on a Bruker Avance III HD spectrometer operated at a frequency of 600 MHz.

## 3. RESULTS AND DISCUSSION

The results of the analyses and their discussion are presented in Table 1.

### 3.1 Elemental Data

From the elemental analysis data in Table 1, with very close percentages of carbon, hydrogen and nitrogen to those calculated, the real ligand as

**Table 1. Physicochemical data for the ligand and the metal complexes**

Compound	Molecular formula	Colour	% Yield	Melting point	Conductance $\mu\text{S mol}^{-1}\text{cm}^{-1}$
HSPy	$\text{C}_{28}\text{H}_{44}\text{N}_2\text{O}_2$	Yellowish-brown	61	106	-----
$\text{La}(\text{SPy})_3 \cdot 2\text{H}_2\text{O}$	$\text{LaC}_{84}\text{H}_{133}\text{N}_6\text{O}_8$	Gray	90	178	10.5
$\text{WO}_2(\text{SPy})_2 \cdot \text{H}_2\text{O}$	$\text{WC}_{56}\text{H}_{88}\text{N}_4\text{O}_7$	Gray	68	310	4.8
% Found (% Calculated)					
	C	H	N		
HSPy	76.21 (76.31)	10.15 (10.06)	6.35 (6.36)		
$\text{La}(\text{SPy})_3 \cdot 2\text{H}_2\text{O}$	67.47 (67.53)	8.72 (8.97)	5.50 (5.63)		
$\text{WO}_2(\text{SPy})_2 \cdot \text{H}_2\text{O}$	59.50 (60.42)	8.10 (7.97)	5.00 (5.03)		

well as its La(III) and W(VI) were prepared and, in solution, the mode of interactions between the metal ions and the ligand are in the mole ratios of La:SPy = 1:3, and  $\text{WO}_2$ :SPy = 1:2; with the association of water molecules. The complexes conform to the general molecular formula  $\text{La}(\text{SPy})_3 \cdot 2\text{H}_2\text{O}$  and  $\text{WO}_2(\text{SPy})_2 \cdot \text{H}_2\text{O}$ .

### 3.2 Conductivity Measurements

The conductivity measurements on both the ligand and the metal complexes ( $10^{-3}$  M) dissolved in acetone gave the values lower than  $30 \mu\text{S mol}^{-1}\text{cm}^{-1}$ , showing that they do not have mobile ions, and that the ligands are bound to the metal centres through strong electrostatic interactions, and chelation effects, giving rise to low conductivity and high melting points. No values were observed for the ligand, indicating its pure covalent nature. The  $\text{WO}_2^{2+}$  complex has a value of  $4.8 \mu\text{S mol}^{-1}\text{cm}^{-1}$  which is lower than that of the  $\text{La}^{3+}$  complex ( $10.5 \mu\text{S mol}^{-1}\text{cm}^{-1}$ ). This could be a result of the two oxo (O=W=O) groups in its coordination sphere which tend to decrease the electronegativity difference of the

metal ion and the anionic ligand further, thus making the complex more covalent than it could have been and reducing its ability to form mobile ions, culminating into its lower conductance. Similar observation had been reported elsewhere [13].

### 3.3 Melting Points

Both complexes have higher melting point values than the ligand. This further confirms the more covalent nature of the ligand as was observed in their conductivities, since more covalent compounds have relatively lower melting points. Tungsten complex has a higher value of  $310^\circ\text{C}$  unlike its lanthanum analogue with  $178^\circ\text{C}$ . The big difference could result from the two oxo (O=W=O) groups in its coordination sphere which could attract neighbouring hydrogen atoms to form hydrogen bonding.

### 3.4 Solubility Data

The solubility data of the ligand and the metal complexes are shown in Table 2.

**Table 2. Solubility data of the HSPy ligand and its metal complexes in various solvents**

Solvent	HSPy	$\text{La}(\text{SPy})_3 \cdot 2\text{H}_2\text{O}$	$\text{WO}_2(\text{SPy})_2 \cdot \text{H}_2\text{O}$
Ethylacetate	vs	vs	vs
Chloroform	s	ss	s
Petroleum ether	ss	is	ss
Toluene	vs	s	is
Methanol	is	is	is
n-hexane	ss	ss	ss
Cyclohexanol	vs	vs	s
Propan-2-ol	ss	s	s
Ethanol	ss	is	is
Diethylether	s	s	s
Acetone	vs	vs	vs
DMSO	vs	vs	vs
Dioxane	vs	vs	vs
Water	is	is	is
Benzene	s	ss	ss
Pyridine	vs	vs	vs

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

The solubility data in Table 2 show that the ligand and the complexes are hydrophobic which means that the distribution of these complexes from aqueous media into organic media in which they are slightly soluble (such as acetone, ethylacetate, chloroform, dioxane, benzene, etc) is favourable. The complexes showed greater degrees of solubility in ethylacetate, acetone, DMSO, dioxane and pyridine, with more alkyl or aromatic functionality and additional donor groups.

In effect, these solvents can be used together with other inert organic solvents such as chloroform (CH<sub>3</sub>Cl) and carbon tetrachloride (CCl<sub>4</sub>) 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 [14, 15].

Further, it is interesting to note that the W complex is insoluble in toluene but the La complex is, even when both complexes are slightly soluble in benzene. This could be attributed to a greater hyperconjugation of the toluene with the La complex than with the W complex when attached.

### 3.5 Electronic Spectra

The electronic spectral data of the ligand and the metal complexes are given in Table 3.

The absorption maxima  $\lambda_1$  and  $\lambda_2$  occurred in the spectral data of both the ligands and the metal complexes, at between 325-328 nm and 358-364 nm respectively, in the near ultraviolet region. The values for  $\lambda_1$  (lower values) are ascribed to  $\pi \rightarrow \pi^*$  transition which is of higher energy, therefore smaller wavelengths; while those for  $\lambda_2$  are attributed to the  $n \rightarrow \pi^*$  transition which has lower energy and higher wavelengths. The similar values for the ligand and the metal complexes suggest that the  $\pi$ -bonding system in the ligand is almost intact in the ligand anion of the metal complexes [16,5]; indicating that there is no interaction between the metal ions and the  $\pi$ -bonding system of the ligand. Therefore, the coordination (interaction) between the metal ions and the ligand is mainly through  $\delta$ -bond formation between metal ions ( $M^{n+}$ ) and the oxygen atoms of the carbonyl group (C=O) of the ligand.

### 3.6 Infrared Spectra

The infrared spectra for the ligand and complexes are shown in Figures 3(a-c).

Table 3. Electronic spectral data of the ligand and the metal complexes

Ligand/complexes	$\lambda_1$ max (nm)	$\epsilon_1$ (L.mol <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_2$ max (nm)	$\epsilon_2$ (L.mol <sup>-1</sup> cm <sup>-1</sup> )
HSPy	327	$1.48 \times 10^4$	360	$3.5 \times 10^4$
La(SP <sub>3</sub> ) <sub>3</sub> .2H <sub>2</sub> O	325	$4.6 \times 10^3$	358	$1.2 \times 10^4$
WO <sub>2</sub> (SP <sub>2</sub> ) <sub>2</sub> .H <sub>2</sub> O	328	$2.6 \times 10^4$	364	$1.9 \times 10^4$

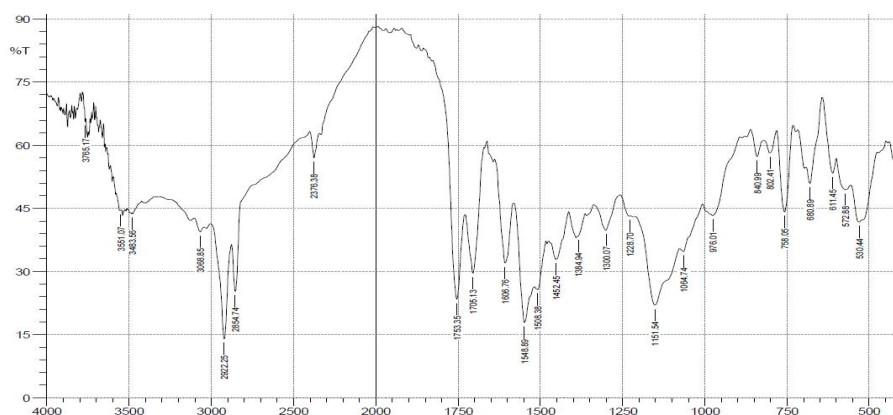


Figure 3(a). IR spectrum of 1-phenyl-3-methyl-4-stearoylpyrazol-5-one, (HSPy)

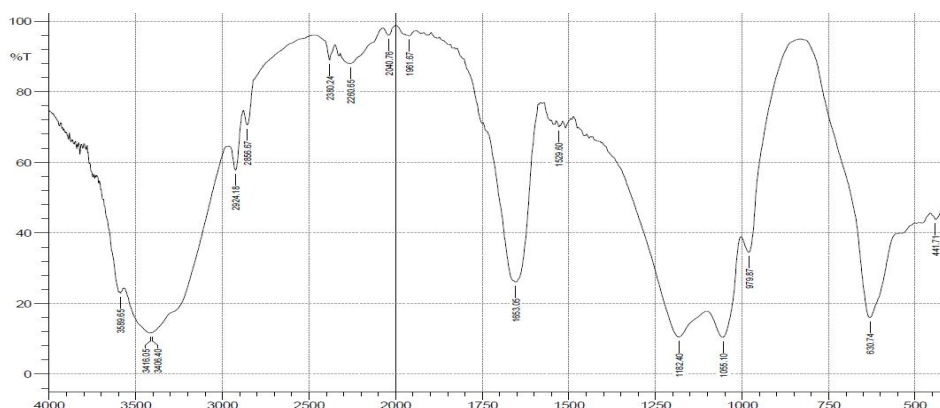


Figure 3(b). IR spectrum of La(SPy)<sub>3</sub>.2H<sub>2</sub>O

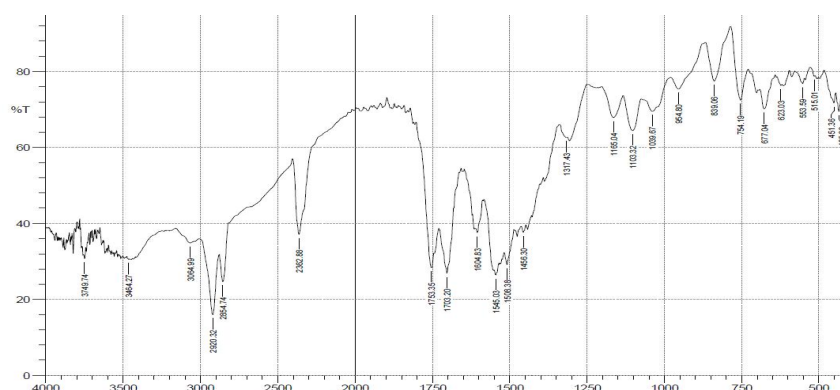


Figure 3(c). IR spectrum of WO<sub>2</sub>(SPy)<sub>2</sub>.H<sub>2</sub>O

The observed IR frequencies have been assigned by comparison with those of previous reports on 4-acylpyrazolones-5 and their metal complexes [8,12]. The intense peak at 3551 cm<sup>-1</sup> of the ligand is assigned to the νO-H frequency of the enol form of the ligand [9]. It 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. Similar broad bands centred 3416 cm<sup>-1</sup> and 3464 cm<sup>-1</sup> in the IR of the La(III) and W(VI) complexes respectively, 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 [15].

The band spectra occurring at 1600–1700 cm<sup>-1</sup> 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. The IR spectra of the ligand exhibited two sets of C=O vibrational frequency bands at 1753 cm<sup>-1</sup> (strong) and 1705 cm<sup>-1</sup>. The W(VI) complex showed a similar but very weak band at the same 1753 cm<sup>-1</sup>, indicating the presence of a modified form of -C=O group. However, the relative band observed at 1705 cm<sup>-1</sup> in the ligand shifted to higher frequencies relative to similar absorbances of the metal complexes; La(SPy)<sub>3</sub> = 1653 cm<sup>-1</sup> and WO<sub>2</sub>(SPy)<sub>2</sub> = 1703 cm<sup>-1</sup>. The bands obtained at 1604 and 1545 cm<sup>-1</sup> for the WO<sub>2</sub>(SPy)<sub>2</sub>.H<sub>2</sub>O complex matched well with the values 1603 and 1568 cm<sup>-1</sup> obtained for [MoO<sub>2</sub>(R)<sub>2</sub>] (where R = alkyl based derivatives other than stearyl) matching well with complexation [17] considering that both Mo and W are in the same Group (6) in the periodic table. The strong broad IR bands at around 1653 and 1529 cm<sup>-1</sup> in the La(SPy)<sub>3</sub>.H<sub>2</sub>O complex match well with the IR spectra of the Tb analogue which showed bands at around 1650

and  $1550\text{ cm}^{-1}$  [18]. Upon complexation of these ligands to the metal or center there could be a degree of resonance delocalization occurring, giving the broadened IR resonances. Similar observation had been reported for other quinones of lanthanide(III) species [19].

The symmetric stretching frequency bands of the C=O vibrations appeared as medium bands at  $1385\text{ cm}^{-1}$  in the IR spectra of the ligand, but were not observed in the complexes. This is an indication of the involvement of the C=O in complexation with the metal ions and formation of the C=O-M bonding system. Similar reports had been recorded [5,8,10].

The unique absorption bands appearing near  $954\text{ cm}^{-1}$  in the IR of the  $\text{WO}_2(\text{SPy})_2$  alone have been attributed to the O=W=O while the bands at  $441$  and  $436\text{ cm}^{-1}$  present in  $\text{La}(\text{SPy})_3$  and  $\text{WO}_2(\text{SPy})_2$  respectively have been assigned to  $\nu(\text{La-O})$  and  $\nu(\text{W-O})$ . Such bands are absent in the IR of the ligand, indicating coordination with the metal ions via deprotonation.

### 3.7 Nuclear Magnetic Resonance (NMR) Spectra

#### 3.7.1 The proton ( $^1\text{H}$ ) NMR

The  $^1\text{H}$  NMR spectral data of the free ligand and the complexes in DMSO as solvent at a frequency of 600 MHz are shown in Figures 4(a-c).

The results show all the expected resonances for 1-phenyl-3-methyl-4-acylpyrazol-5-ones the integration of the signals being in accordance with the formulae proposed. The HSPy showed  $^1\text{H}$  NMR resonance peak at 3.65 ppm (Figure 3(a)), for the -OH group. This shows that the

enolic form of the ligand was prepared. This signal was absent in the spectra of the complexes, indicating complexation via deprotonation of the enolic hydrogen of the ligand. Similar observation had been reported elsewhere [20]. The formation of metal complexes is further confirmed by the broad phenyl proton signals observed in the metal complexes (Figures 4 b and 4 c). This corroborates the reports of Pariya and Theopold, which stated that the presence of unpaired electrons results in a large isotropic shift and severely broadened resonances which usually obscure any nuclear spin-spin coupling and make the integration of signals difficult [21].

The signals of methyl and methylene protons observed as multiplets at 0.48–2.15 ppm in HSPy had been always found shifted to higher fields; at 0.86-1.48 ppm and 0.82 -1.17 ppm for the  $\text{La}(\text{SPy})_3$  and  $\text{WO}_2(\text{SPy})_2$  metal complexes respectively, upon coordination with metal ions, as shown in Figures 4(a-c). This indicates non-uniform interactions of the oxygen atoms coordinated to the metal ions, an indication of the involvement of the carbon atoms bonded to these oxygen atoms in the effective complexation and formation of strong C—O—M bonds through electron delocalization. Similar observation had been reported elsewhere [20].

On the other hand, the signals of the phenyl protons observed as resonance peaks at 6.84 – 7.42 ppm for the HSPy have always been shifted to downfields at 7.60-7.81 ppm and 7.33–7.72 ppm for the  $\text{La}(\text{SPy})_3$  and  $\text{WO}_2(\text{SPy})_2$  metal complexes respectively, upon coordination with the metal ions. Again, this indicates formation of metal complexes and chelates between the ligand and the metal ions, in line with the reports of Rani [21].

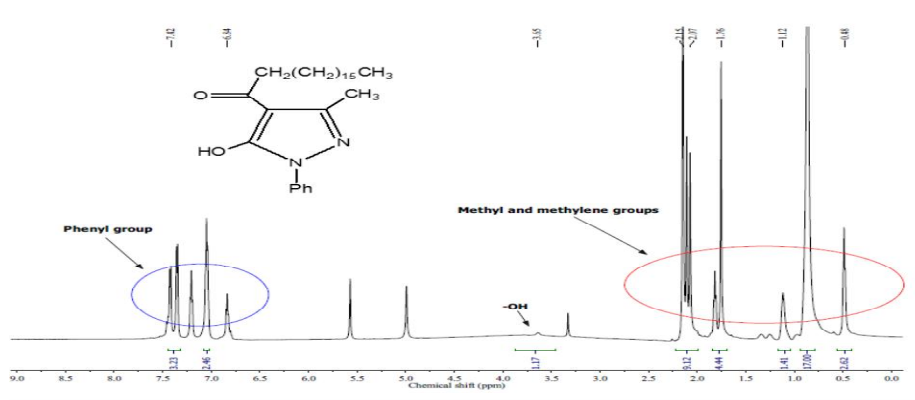
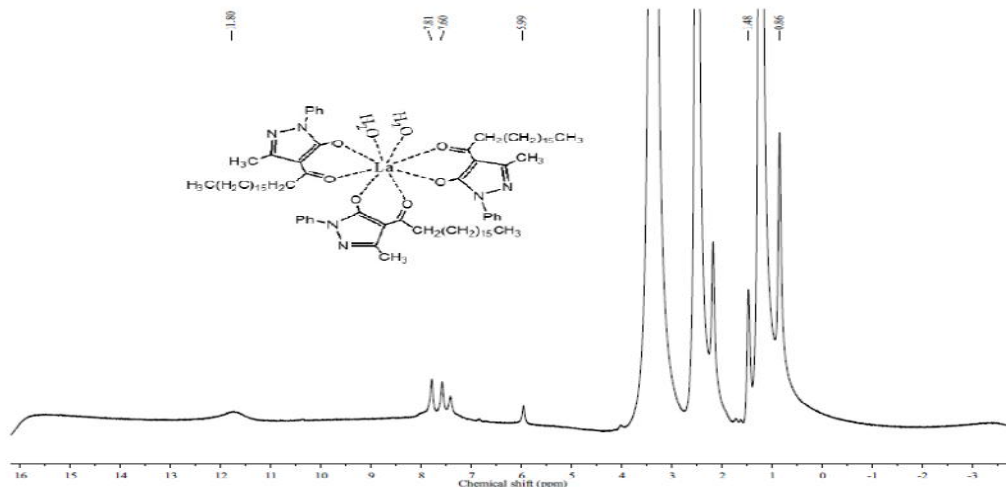
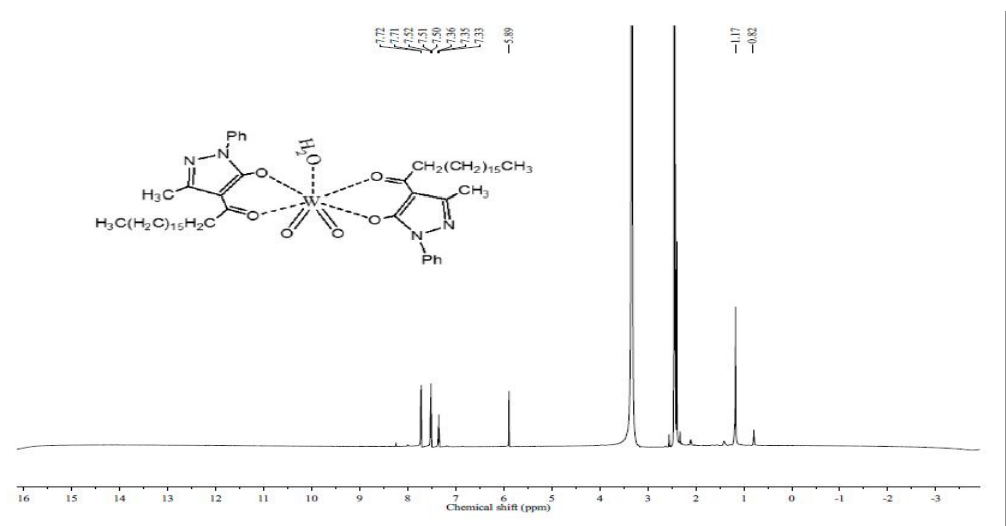


Figure 4(a).  $^1\text{H}$  NMR spectrum of HSPy

Figure 4(b).  $^1\text{H}$  NMR spectrum of  $\text{La}(\text{SPy})_3 \cdot 2\text{H}_2\text{O}$ Figure 4(c).  $^1\text{H}$  NMR spectrum of  $\text{WO}_2(\text{SPy})_2 \cdot \text{H}_2\text{O}$ 

### 3.7.2 Carbon-13 ( $^{13}\text{C}$ ) NMR

The  $^{13}\text{C}$  NMR spectral data of the free ligands and the complexes in DMSO at a frequency of 600 MHz are shown in Figures 5(a-c).

Analyses of the  $^{13}\text{C}$  NMR spectral data indicate that the carbon resonance spectra of  $\text{C}=\text{O}$  observed at 174.50 ppm for the HSPy (Figure 5 a) are shifted upfield very slightly to 174.51 ppm in  $\text{La}(\text{SPy})_3 \cdot 2\text{H}_2\text{O}$  (Figure 5b), and obscured in  $\text{WO}_2(\text{SPy})_2 \cdot \text{H}_2\text{O}$  as shown in Figure 5(c). Similar results for the ligand and the

$\text{La}(\text{SPy})_3 \cdot 2\text{H}_2\text{O}$  could indicate that the degree of resonance stabilization across the O-C-C-C-O bite is less for the La species and possibly some partial dissociation of the ligand occurred (namely the  $\text{C}=\text{O}$  may not be coordinating at all times to La), potentially explaining why La complex is generally more soluble than W one. This is an indication that the carbon atoms of the C-O-M bonds are shielded in the metal complexes, and may indicate weak CO-M bonds [10,20,21]. This is probably due to the involvement of these carbon atoms in the chelation process through electron delocalization.



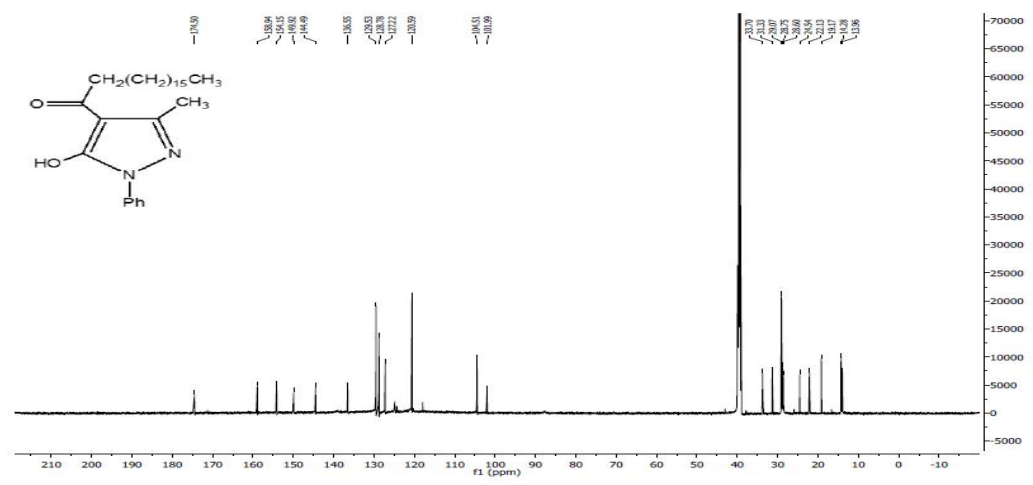


Figure 5(a).  $^{13}\text{C}$  NMR spectrum of HSPy

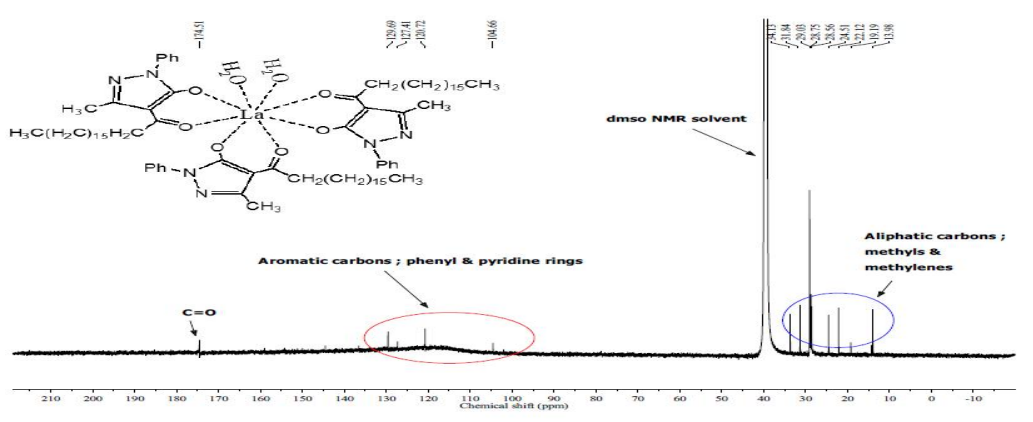


Figure 5 (b).  $^{13}\text{C}$  NMR spectrum of  $\text{La}(\text{SP})_3 \cdot 2\text{H}_2\text{O}$

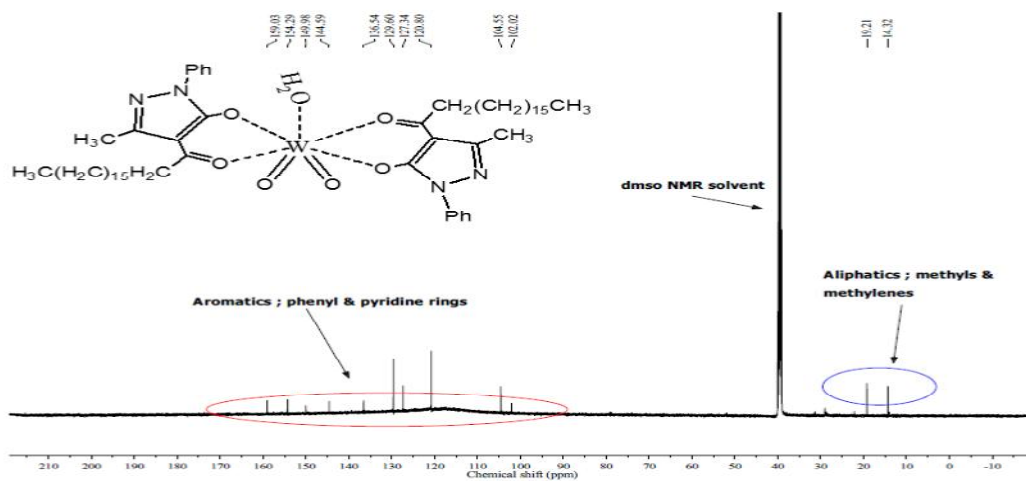


Figure 5 (c).  $^{13}\text{C}$  NMR spectrum of  $\text{WO}_2(\text{SP})_2 \cdot \text{H}_2\text{O}$

#### 4. CONCLUSION

The analytical data show that the compositions or stoichiometries of the complexes formed between the metal ions and the ligand are in the mole ratios of La:SPy = 1:3, and  $\text{WO}_2$ :SPy = 1:2; with the association of water molecules. Therefore, the complexes conform to the general molecular formula  $\text{La}(\text{SPy})_3 \cdot 2\text{H}_2\text{O}$  and  $\text{WO}_2(\text{SPy})_2 \cdot \text{H}_2\text{O}$ .

The coordination or mode of interaction between the metal ions and the ligand is mainly through  $\delta$ -bond formation between metal ions ( $\text{M}^{III}$ ) and the oxygen atoms of the carbonyl group ( $\text{C}=\text{O}$ ) of the ligand, resulting in the chelate formation through  $\text{C}-\text{O}-\text{M}$  bond, via the deprotonation of the enolic hydrogen ( $-\text{OH}$ ) of the ligand. This is analogous to the butanoyl homologue reported by Ehirim *et al* [5]; however, the degree of

alkylation affected the physical properties such as the melting points in which the more alkylated stearyl homologue had higher values, probably due to more intermolecular activities; but lower conductivities depicting more covalence; as a result of the longer alkyl chain.

From the results of the analyses, the expected structures of the metal complexes are proposed, as shown in Figures 6(a) and 6(b).

The proposed structures are in line with the structures of the 1-phenyl-3-methyl-4-stearylpyrazol-5-one (HQ) complexes of rare-earth metals (Eu, Gd, and Tb) of the composition  $[\text{Ln}(\text{Q})_3(\text{H}_2\text{O})(\text{EtOH})]$ ; ( $\text{Ln}$  = lanthanide element, any of Eu, Gd, and Tb) and the Tb analogue with the presented La complex being isolated as  $[\text{Tb}(\text{SPy})_3(\text{H}_2\text{O})_2]$  [18].

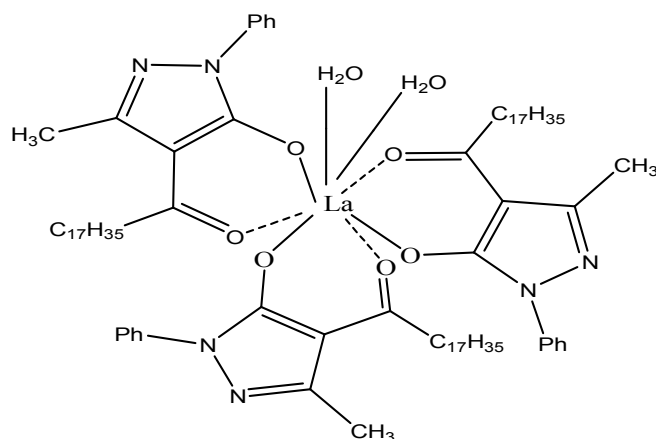


Figure 6 (a). Structure of  $[\text{La}(\text{SPy})_3 \cdot 2\text{H}_2\text{O}]$ ; eight coordinate

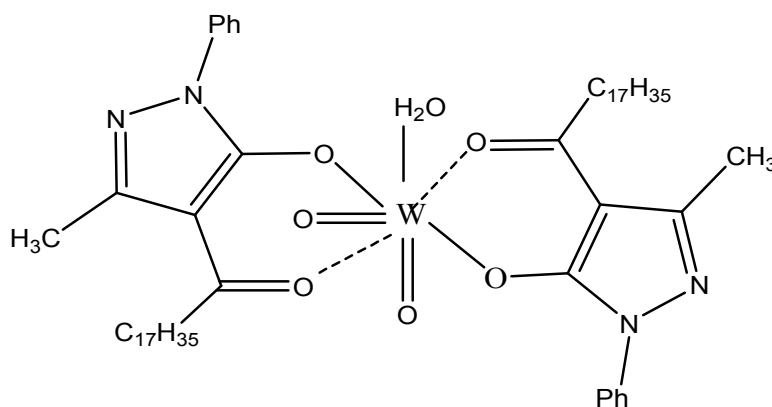


Figure 6 (b). Structure of the tungsten-pyrazolone derivative,  $[\text{WO}_2(\text{SPy})_2 \cdot \text{H}_2\text{O}]$ ; seven coordinate

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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