

## SHORT COMMUNICATION

# SPECTROSCOPIC STUDIES OF Th(IV), La(III) and Pb(II) COMPLEXES OF 4-TRIFLUOROACETYL AND 4-TRICHLOROACETYL DERIVATIVES OF 3-METHYL-1-PHENYLPYRAZOL-5-ONE

B.A. UZOUKWU<sup>1</sup> and P.U. ADIUKWU<sup>2</sup>

<sup>1</sup> Department of Pure and Industrial Chemistry, University of Port Harcourt, Port Harcourt, Nigeria.

<sup>2</sup> Rivers State University of Science and Technology, Port Harcourt, Nigeria.

(Received: 17 July 1995; accepted: 10 June 1996)

**Abstract:** Thorium(IV), Lanthanum(III) and Lead(II) complexes of 4-trifluoroacetyl and 4-trichloroacetyl derivatives of 3-methyl-1-phenylpyrazol-5-one have been synthesised and characterized by elemental, UV, IR, <sup>1</sup>H and <sup>13</sup>C NMR spectral studies. Spectral analyses show that the complexes are dehydrated and have the general molecular formula ML<sub>n</sub>, where M(n) = Th(4), La(3) and Pb(2). The analyses further showed that the CO-M bond of metal-trifluoroacetylpyrazolonate complexes are weaker than the metal-trichloroacetylpyrazolonate complexes.

**Key words:** Complexes, IR, Lanthanum, Lead, ligands, NMR, Thorium, 4-trihaloacetyl-3-methyl-1-phenylpyrazol-5-one, spectroscopy, UV.

## INTRODUCTION

There is much interest in applying 4-acyl-3-methyl-1-phenylpyrazolones for solvent extraction<sup>1-4</sup> of metals from acid solution. Recent<sup>3-6</sup> successes in this area have revealed the potential application of this class of chelating agents in the separation of metals from aqueous media. There is a need to understand the mechanism of interaction of these ligands with metal ions in solution and to obtain their structural and spectroscopic properties. The Th(IV), La(III) and Pb(II) complexes of these ligands (Fig. 1) have therefore, been isolated and studied.

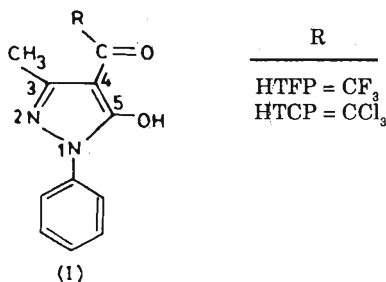


Figure 1: Structure of ligands.

## METHODS AND MATERIALS

**Reagents:** All chemicals used were of analytical reagent grade. The 4-trifluoroacetyl (HTFP) and 4-trichloroacetyl (HTCP) derivatives of 3-methyl-1-phenylpyrazol-5-one were prepared by methods described elsewhere<sup>7</sup> and twice recrystallized from aqueous ethanol.

**Preparation of metal complexes:** The metal salt (5 mmol  $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ ) was dissolved in 80 ml water with warming. This was slowly added with stirring to a warm 80 ml ethanol solution of ligand in a metal-ligand mole ratio of 1:2, 1:3 and 1:4 for Pb(II), La(III) and Th(IV) respectively. The precipitates formed immediately and were separated by filtration after washing with aqueous ethanol (1:1). The products were recrystallized from aqueous ethanol (1:4), dried in air and stored in a desiccator.

Electronic spectral measurements were made with a Pye Unicam PU8700 series uv-visible spectrophotometer. Conductance measurements were made with a Philips PW 9506 conductivity meter. The IR spectral measurements were made on nujol mull and CsI discs using a Perkin Elmer 598 spectrophotometer. The  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectral data were obtained using BRUKER DATA WPAT 80 while  $^{13}\text{C}$  NMR spectral data were obtained using the WUM 360 model.  $\text{CDCl}_3$  was used as solvent. The elemental analyses for C, H and N of the compounds were carried out at the University of Sussex, England.

## RESULTS AND DISCUSSION

The analytical data presented in Table 1 indicate that the complexes conform to a general molecular formula  $\text{ML}_n$  where  $\text{M}(n) = \text{Th}(4), \text{La}(3)$  and  $\text{Pb}(2)$ . It further shows that the complexes do not have any water of crystallization. Conductance measurements on the complexes in DMF gave values lower than  $30 \text{ S} \cdot \text{mol}^{-1} \text{ cm}^2$  showing that none of the complexes are ionic.

### UV and IR spectral analyses

The electronic spectral data of the complexes are presented in Table 1 and are compared with those of the ligands published elsewhere.<sup>8</sup> The absorption maxima  $\lambda_1$  and  $\lambda_2$  occur in the spectra of both the ligands and the three metal complexes. This absorption is assigned intraligand  $\pi \rightarrow \pi^*$  transition. Although all the complexes are pale yellow no absorption bands were recorded in the visible region of any of the complexes for 0.001M concentration of the complexes studied.

The IR data show that broad bands at  $3400 \text{ cm}^{-1}$  (HTFP) and  $3100 \text{ cm}^{-1}$  (HTCP) assigned to  $\nu \text{ OH}$  of the enolic form of the ligand shown in Figure 1 are absent

in the spectra of all the metal complexes indicating that the OH group of the ligand has been deprotonated. The weak broad bands near  $2650\text{ cm}^{-1}$  in the spectra of the ligands assigned to  $\nu$  as  $\text{OH}\cdots\text{O}$  are absent in the spectra of the complexes confirming the conclusion made above. The formation of  $\text{C}\equiv\text{O}-\text{M}$  bonding system is indicated by the shift of  $\nu\text{C}=\text{O}$  from  $1630\text{ cm}^{-1}$  (HTFP) and  $1640\text{ cm}^{-1}$  (HTCP) to  $1610\text{--}1625\text{ cm}^{-1}$  in the IR spectra of the metal complexes (Table 1). It is pertinent to note that the shift in  $\nu\text{C}=\text{O}$  of  $\text{Th}(\text{TFP})_4$  occur by  $5\text{ cm}^{-1}$  which when compared with shifts by  $10\text{--}20\text{ cm}^{-1}$  observed in other complexes may be indicating that  $\text{C}\equiv\text{O}-\text{Th}$  bond of Th-TFP complex is relatively weaker. Absorption bands lower than  $400\text{ cm}^{-1}$  present in the spectra of the metal complexes (Table 1) and absent in spectra of the ligands have been assigned  $\nu\text{M}-\text{O}$ . The trend of  $\nu\text{M}-\text{O}$  in M-TCP complexes follow the order  $\text{La} < \text{Pb} < \text{Th}$ , which is the order of increase in atomic mass of one metal. This observation is contrary to another observation presented in an earlier publication<sup>8</sup> in which the  $\nu\text{M}-\text{O}$  increased with decrease in atomic mass of metal. The present observation has shown that a combination of various factors such as atomic charge, ionic radius and atomic mass of metal ion in a complex may be playing vital roles in determining the trend of the stability of  $\nu\text{M}-\text{O}$  stretching frequencies for a series of metal complexes. This may explain the trend of  $\nu\text{M}-\text{O}$  of M-TFP complexes which follow the order  $\text{La} < \text{Th} < \text{Pb}$  instead.

### NMR spectral analyses

Proton NMR spectral results show that the  $^1\text{H}$  NMR signals assigned to OH group of the ligands were absent in the spectra of the metal complexes, indicating that the OH group was deprotonated.

Results of  $^{13}\text{C}$  NMR spectral data show that the methyl protons C(1) (see Fig. 1) experienced downfield shift by  $\sim 1\text{ ppm}$  in the metal complexes when compared with those of the ligands. Downfield shift by a magnitude of  $1.5\text{--}3.0\text{ ppm}$  are also observed in the  $^{13}\text{C}$  resonance of C(3), C(4) and C(5) atoms of the M-TCP complexes. This is an indication of the involvement of these carbon atoms in effective complexation and formation of strong  $\text{C}\equiv\text{O}-\text{M}$  bonds through electron delocalization. However, in the M-TFP complexes a downfield shift in the  $^{13}\text{C}$  resonance was observed with only C(3) and C(5) atoms. An upfield shift by  $\sim 5\text{ ppm}$  was observed with C(4) indicating that this atom is shielded in the metal complexes. We are suggesting that this is an indication that  $\text{C}\equiv\text{O}-\text{M}$  bond is weaker in M-TFP complexes than in M-TCP complexes. It has been pointed out earlier from IR spectral studies that  $\text{CO}-\text{Th}$  bond of Th-TFP complex is probably weaker than those of other complexes. It is hereby concluded that the stability of  $\text{CO}-\text{M}$  bonds follow the trend  $-\text{CF}_3 < -\text{CCL}_3$  which is the direction of decrease in electronegativity of the trihaloacetyl substituent.

Table 1: Analytical and spectral data of the Th(IV), La(III) and Pb(II) complexes.

Compound (Colour)	Melting point °C	Found (Calc.)/%			$\lambda_1$ (nm) ( $\epsilon_1^*$ )	$\lambda_2$ (nm) ( $\epsilon_2^*$ )	methyl moiety (H)** (C)**	$\nu$ C—O $\nu$ M—O ( $\text{cm}^{-1}$ )	*Molar Conductance
		C	H	N					
HTFP (pink)	139	53.11 (53.34)	3.88 (3.36)	10.25 (10.37)	252 (0.14)	294 (1.32)	2.45(s)	14.89 1630	-
Th(TFP) <sub>4</sub> (yellow)	246	43.88 (44.05)	2.24 (2.46)	8.54 (8.56)	251 (1.70)	302 (4.85)	2.27(s)	15.66 1625	360 28.6
La(TFP) <sub>3</sub> (cream)	178	46.04 (45.68)	3.02 (2.56)	8.63 (8.88)	251 (1.77)	292 (6.63)	2.28(s)	16.19 1620	345 17.9
Pb(TFP) <sub>2</sub> (yellow)	280	38.87 (38.66)	2.24 (2.16)	7.76 (7.51)	251 (0.99)	297 (3.49)	2.15(s)	16.22 1610	368 26.9
HTCP (pink)	136	45.10 (45.11)	2.94 (2.84)	8.52 (8.77)	251 (0.27)	295 (1.31)	2.60(s)	17.35 1640	-
Th(TCP) <sub>4</sub> (yellow)	258	38.25 (38.27)	1.99 (2.14)	7.47 (7.44)	252 (1.83)	311 (3.13)	2.48(s)	19.11 1610	400 23.8
La(TCP) <sub>3</sub> (yellow)	170	40.04 (39.50)	2.26 (2.21)	7.71 (7.68)	251 (1.08)	293 (2.59)	2.60(s)	18.15 1614	382 11.9
Pb(TCP) <sub>2</sub> (yellow)	211	33.78 (34.14)	2.00 (1.91)	6.66 (6.64)	251 (0.46)	289 (1.19)	2.50(s)	weak 1613	394 38.7

s, singlet; \*values x 10<sup>-4</sup> l<sup>-1</sup> mol cm; \*\* values in ppm; + values in S.mol<sup>-1</sup> cm<sup>2</sup>;  $\nu$  stretching frequency

The  $^{19}\text{F}$  NMR spectral studies show a single fluorine resonance peak at -66.8 ppm (Th-TFP) relative to -71.0 ppm recorded for the ligand HTFP.

### Acknowledgment

The authors thank International Foundation for Science, Sweden for a grant to B.A.U. and Rivers State University of Science and Technology for support to P.U.A.

### References

1. Mirza M.Y. & Nwabue F.IK. (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. *Radiochimica Acta* **27**: 47-50
2. Coronel F.T., Mareva St. & Yordanov N. (1982). Extraction of uranium(IV) from phosphoric acid solutions with 1-phenyl-3-methyl-4-benzoylpyrazolone-5 (PMBP). *Talanta* **29**: 119-123.
3. Uzoukwu B.A. & Nwachukwu C.K. (1994). Extraction of Mo(VI) from mineral acid solutions using benzene solution of 1-phenyl-3-methyl-4-butyrylpyrazolone-5. *Indian Journal of Chemistry* **33A** : 274-276
4. Uzoukwu B.A. & Okafor E.C. (1990). Extraction of Fe(III) and U(IV) with 1-phenyl-3-methyl-4-acyl-pyrazolones-5 from aqueous solutions of different acids and complexing agents. Separation of Fe(III) from U(VI). *Radiochimica Acta* **51**: 167-172.
5. Ogwuegbu M.O.C. & Oforka N.C. (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.
6. Akama Y., Sato K., Ukaji M. & Kawata T. (1985). Studies on extraction of copper (II) with 1-phenyl-3-methyl-4-acyl-5-pyrazolone. *Polyhedron* **4**: 59-63.
7. Jensen B.S. (1959) The synthesis of 1-phenyl-3-methyl-4-acyl-pyrazolones-5. *Acta Chemica Scandinavia* **13**: 1668-1670.
8. Uzoukwu B.A. (1991). Physicochemical studies of 4-trifluoroacetyl and 4-trichloroacetyl derivatives of 3-methyl-1-phenyl-pyrazol-5-one and their U(VI), Fe(III) and Ca(II) complexes. *Indian Journal of Chemistry* **30A**: 372-374.