Synthesis and Structural Study of Yttrium (III) Complexes with Derivatives of Vitamin K3 Analog

Sanjay Dattatray Gaikwad*

Department of Chemistry, Bharatiya Jain Sanghatana's ASC College, Wagholi, Pune, Maharashtra, **INDIA**
Email: gsanjayin@yahoo.com

_____

ABSTRACT

Yttrium(III) metal forms a new complexes with -chloro, -bromo and -iodo derivative of lawsonemonoxime (2-hydroxy-1,4-naphthoquinone-1-oxime) as[$YL_3(H_2O)_4$] have been synthesized and characterized via Elemental Analysis, TG, IR, ^1H NMR for ligands, Electronic and Magnetic Susceptibility techniques. These complexes are yellow and brown in color. The study showed that the mononuclear behavior of the complex. The bicaped antiprismatic geometry is suggested for all three halolawsonemonoxime complex of Yttrium.

Graphical Abstract

$$YCl_3.6H_2O + 3HL \xrightarrow{\text{EtOH/H}_2\text{O,pH5}} [Y(L)_3(H_2O)_4]$$
$$(HL = HL_1, HL_2 \text{ or } HL_3)$$
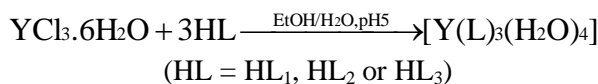
Complex formation

Keywords: Yttrium, Lawsone, halolawsonemonoximes, Yttrium Complex, Thermal Analysis.
_____

INTRODUCTION

The isomeric pair of Lawsone (2-hydroxy-1,4-naphthoquinone) and Juglone (5-hydroxy-1,4-naphthoquinone) are naturally occurring compounds of Vitamin K3 analog. These compounds having importance in various fields like analytical, coordination, medicinal, industrial, pharmaceutical etc. Our aim is to synthesise the halo and oxime derivative of lawsone and its Yttrium complexes. These complexes are studied with IR and UV.

MATERIALS AND METHODS

The Chemicals used in the synthesis of the all ligands and metal complexes were of A. R. Grade. Diclone (2,3-dichloro-1,4-naphthoquinone) and Lawsone (2-hydroxy-1,4-naphthoquinone) were the product of fluka A. G., Switzerland. The halolawsone [3-(-*chloro, -bromo, -iodo*)-2-hydroxy-1,4-naphthoquinone] was synthesized by Fiesers[1] method. The oxime derivative of all halolawsone HL_1, HL_2 and HL_3 (-*chloro, -bromo, -iodo respectively*) (Scheme 1) were synthesized by the method as reported earlier [**1-4**].
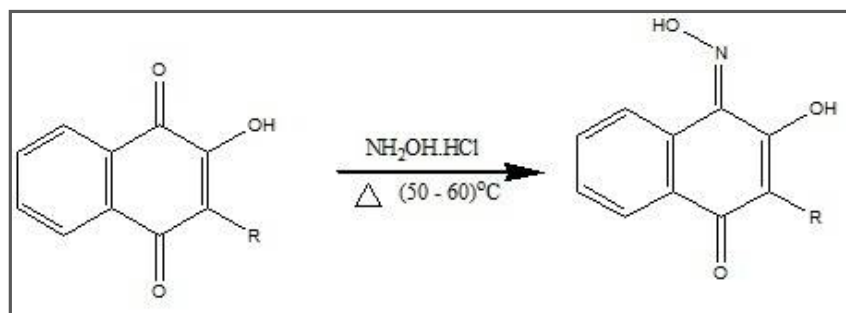
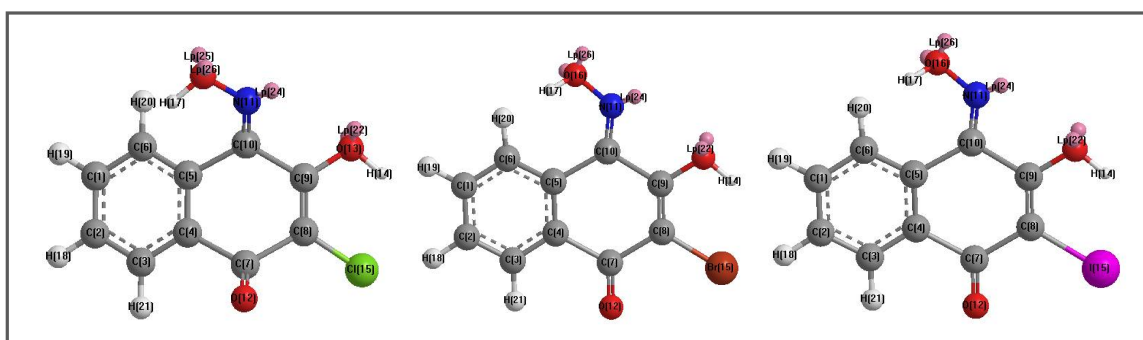**Scheme 1.** Preparation of Oxime derivative

Figure 1. HL1, HL2 and HL3 (R = -chloro, -bromo, -iodo)

Complex preparation [**5**], in a hot solution of 3.00 mmol of ligand in ethanol (25 mL), an aqueous solution of 1.00 mmol of Yttrium (III) hexahydrate (5 mL) was added. After this addition an aqueous ammonia solution (1:20 v v^{-1}) was added drop wise to adjust the pH 5 when the complex started to precipitate. This precipitated mixture was refluxed for 3 h on oil bath. The resultant mixture was cooled and filtered it. The precipitate was washed by distilled cold water and then hot methanol and dried in *vacuo* over fused calcium chloride at ambient temperature.

$$YCl_3.6H_2O + 3HL \xrightarrow{\text{EtOH/H}_2\text{O,pH5}} [Y(L)_3(H_2O)_4]$$
$$(HL = HL_1, HL_2 \text{ or } HL_3)$$
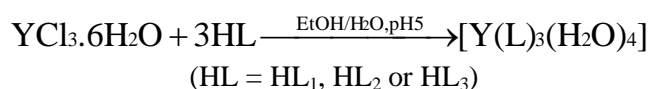
Scheme 2. Complex formation

The complexes and reactants were characterized by their physical constant and TLC behavior with the authentic sample. The elemental analysis were performed by micro analysis using Flash EA, C, H, N and S Analyzer instrument for the percentage of carbon, hydrogen and other elements. The non-isothermal profile of the metal complexes was recorded on a Perkin-Elmer Delta series thermal analysis system, TGA-7 Model with a chromel-alumel thermocouple in air atmosphere up to 700°C with heating rate 10°C min^{-1}. The IR spectra were recorded FTIR Nicolet -5700 in the range of wave number 400-4000 cm^{-1}. The electronic spectra were recorded using Shimadzu UV-300 Spectrophotometer model using 1 cm matched quartz cell in ethyl alcohol. The ^{1}H NMR spectra of ligands were recorded on JEOL – 400 MHz IN CDCl$_3$. The structures of ligands and their Yttrium complexes is simulated by using Cambridge software (ChemOffice 2008-Chem3D ultra 8.0 followed by MM2) for to measure bond length and bond angles.

RESULTS AND DISCUSSION

An aqueous solution of Yttrium chloride hexahydrate ($YCl_3.6H_2O$) react in one pot[6] with an ethanolic solution of HL_1, HL_2 or HL_3 under reflux condition in a 1:3 mole ratio to yield yellowish brown, yellow and radish brown product Y1, Y2 and Y3 respectively (Scheme 2). All these complexes are poorly soluble in non polar solvent, moderately soluble in polar solvents and highly soluble in strongly coordinating solvent. These observations indicate, the all complexes are mononuclear in nature. While most of the complexes of Yttrium(III) are dinuclear behavior [7, 8]. It may suggest the bicaped antiprismaticgeometry [9] for all three halolawsonemonoxime complex of Y, as given in figure 2.
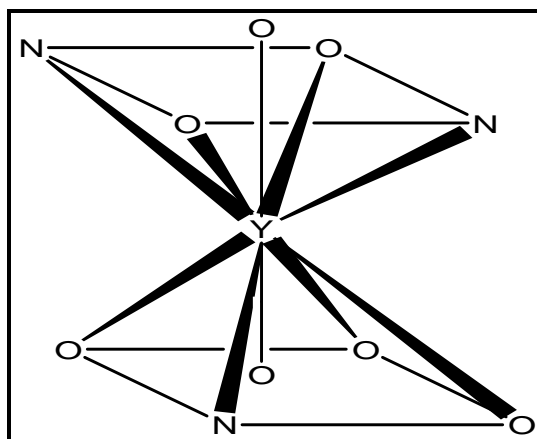

Figure 2. Proposed bicaped antiprismatic geometry for complex.

All three halolawsonemonoxime complexes Y1 to Y3 have four coordinated water [10] molecules. The analytical data of the complexes is compiled in table 1.

Table 1. Analytical and Physicochemical data of the complex

Stoichiometry	Color	Yield %	Decomp. Temperature °C	Element (%)				S mol^{-1} cm^2
				C	H	N	M	
$C_{30}H_{23}O_{13}N_3Cl_3Y$ (Y1)	Brownish Yellow	77	225	43.72	2.85	4.90	10.37	2.9
$C_{30}H_{23}O_{13}N_3Br_3Y$ (Y2)	Brown	76	220	38.08	2.41	4.00	9.70	1.9
$C_{30}H_{23}O_{13}N_3I_3Y$ (Y3)	Radish Brown	76	230	33.09	2.10	3.93	7.98	1.3

All these complexes have decomposes in the range of 220 to 230°C. The molar conductance values 2.1 and 3.2 mho mol^{-1} cm^2 of the complex in DMSO indicates their non electrolytic nature [11]. It gives monobasic behavior of these ligands in complex.

Thermogravimetric Studies: The data of nonisothermal thermodynamic profile for the solid phase thermal decomposition of complexes is summarized in table 2. Three step weight loss pattern is observed for all complexes [12]. It may be due to crowding around the Yttrium metal. Two step weight loss pattern is observed in Yttrium complex with lawsonemonoxime and phthiocolmonoxime [5]. The kinetic parameters for these thermal decomposition reactions are calculated from the programms based on Coats and Redfern [13] are summarized in table 3. Among these three steps, the first step starts from 130, 155 and 165°C respectively in Y1, Y2 and Y3 complexes. It is attributed to loss of coordinated water molecule, it require activation energy 86 to 107 kJ mole^{-1} i.e., 21-26 kJ mole^{-1} for each water molecule. The order of dehydration reaction 1.60, 3.50 and 1.68 is observed for the Y1, Y2 and Y3 complexes respectively. It may due to they are thermally more stable. The thermal

stability is observed in the order [14] of Cl<Br<I. The second step has resulted in to accelerated weight loss pattern within a very narrow temperature range 10 to 15°C, then it gives stable polymeric compound [**5**] $(YL_2)_n$. Above 315°C temperature, the third step starts. It attributes to decomposition of one of the ligand.

Table 2. Thermal Analysis Data

Steps	Complexes (temperature range & % loss)			Assignment
	Y1	**Y2**	**Y3**	
I	130-225	155-220	165-235	Dehydration
	8	7	7	
II	225-230	220-235	235-250	Sharp decomposition of one of the Ligand
	27	34	28	
III	315-558	325-605	325-585	Decomposition of remaining Ligand
	53	47	55	

Table 3. Kinetic parameters

Complexes	Temp. Range in (°C) or stages of decomposition	Weight Loss (%)	Order of reaction (n)	Activation Energy (KJ mole^{-1})
Y1	130-225	8	1.60	86.89
	315-558	53	1.43	56.05
Y2	155-220	7	3.50	107.7
	325-605	47	2.14	70.02
Y3	165-235	7	1.68	97.53
	165-235	55	2.13	70.22

Infrared Study: The significant IR absorptions are given in table 4. It is observed that, the υ(O-H) frequency at 3100 cm^{-1} disappears after complex formation. The broad band observed in the region 3300-3200 cm^{-1} due to υ(O-H) of oxime group and coordinated water molecule. The small band observed at 3648 cm^{-1} in the spectrum of Y2. It is due to presence of lattice water. The IR absorption for υ(C=O), υ(C=N) and υ(C-X) are shifted to lower value are due to complex. It may be due to delocalization of electron density. While the absorption for υ(C-O) and υ(N-O) shifted to higher value. It may be due to bonding between Metal. The frequency at ~ 454- 468 cm^{-1} is observed for new Y-O (Table 4).

Table 4. Significant IR absorption[a]

Complexes			Assignments
Y1	**Y2**	**Y3**	
3250,3112 (3412.3375,3100)	3648,3275 (3325,3200,3100)	3237,3151 (3325,3187,3100)	υ (O-H)
1580 (1605)	1581 (1615)	1584 (1620)	υ (C=O)
1522 (1577)	1514 (1586)	1537 (1583)	υ (C=N)
1224 (1211)	1223 (1213)	1222 (1216)	υ (C-O)
1059 (1051)	1060 (1046)	1051 (1048)	υ (N-O)
691 (695)	690 (693)	688 (706)	υ (C-X)
454 (---)	468 (---)	464 (---)	υ (Y-O)

[a]values in parentheses correspond to Ligand

Electronic spectral study: The electronic spectra of ligand and their complex with Yttrium metal were done in solvents like methanol, acetonitrial and dimethyl sulphoxide. The four peaks are observed in every spectrum. The peak first and third are attributed to benzenoid electron transferred [**14**], second peak is for quinonoied electron transferred and fourth shoulder peak is for n-π* transition or Ligand to metal charge transfer. All these peaks shift to higher value after complex formation.

Table 5. Robustness data of the proposed method

Parameter varied	Retention time	Peak area	Plate count	Tailing factor	Resolution
Sacubitril					
Flow rate – 0.9 mL min^{-1}	2.585	1706394	4447	1.37	-
Flow rate – 1.1 mL min^{-1}	3.892	2593791	6230	1.42	-
Column temperature-23°C	2.585	1691461	4319	1.37	-
Column temperature-27°C	3.888	2591384	6128	1.40	-
Valsartan					
Flow rate – 0.9 mL min^{-1}	3.015	1166535	3148	1.51	2.29
Flow rate – 1.1 mL min^{-1}	4.494	1758852	4216	1.53	2.44
Column temperature-23°C	3.023	1160898	3106	1.54	2.29
Column temperature-27°C	4.488	1770765	4117	1.54	2.42

APPLICATION

The study showed that the mononuclear behavior of the complex.

CONCLUSION

1. New Complexes of Yttrium with halolawsonemonoximes.
2. The complexes are studied with IR, UV and thermal.
3. The bicaped antiprismaticgeometry is suggested for Y complexes.

ACKNOWLEDGEMENTS

REFERENCES

[1]. L. F. Fieser, *J. Bio. Chem.*, **1940**, 133, 391.

[2]. S. D. Gaikwad, D. G. Kanse, V. D. Kelkar and B. A. Kulkarni, *Sunth. React. Inorg. Met. Org. Chem.*, **1996**, 26(9), 77-87.

[3]. S. D. Gaikwad, *Intern. J. Curr. Chem. Sci.*, **2015**, 9 (5), 1-4.

[4]. F. Radt, *"Elsevier's Encyclopaedia of Organic Chemistry"* Series III, 12B (**1952**) .

[5]. S. D. Gaikwad, *Res. J. Chem. Env.*, 2012, 16(4), 35.

[6]. S. D. Gaikwad, *J. Applicable Chem.*, 2013, 2(5), 1262.

[7]. P. Constantina, G. E. Constantinos, P. R. Catherine, T. Aris, M. Evy, P. Spyros, *Spectrochimica Acta Part A*, 2008, 70, 718- 728.

[8]. C. J. Milions, T. C. Stamatatos, P. Kyritsis, A. Terzis, C. P. Raptopoulou, R. Vicente, A. Escuer, S. P. Perlepes, *J. Inorg. Chem.,* **2004**, 2885.

[9]. M. D. Grillone, f. Benetollo and G. Bombiri, *Polyhedron*, 1991, 18(10), 2171.

[10]. F. A. Miller and C. H. Wilkins, *Anal. Chem.*, 1952, 24, 1253 (**DOI:** 10.1021/ac60068a007.

[11]. K. K. Narang, T. R. Rao, Sabita. Shrestha, Shankar Shrestha, *Synt. React. Inoerg. Met. Org. Chem.*, 2000, 30(5), 931.

[12]. S. Y. Rane, S. B. Padhye, G. N. Natu, A. H. Kumar, E. M. Khan, *J. Therm. Anal.*, 1989, 35, 2331

[13]. A. W. Coats, J. P Redfern, *Nature*, 1964, 201, 68

[14]. F. V. Dandawate, J. G. Kodilikar, V. D. Kelkar, B. A. Kulkarni, *Thermochim. Acta*., **1994**, 241, 103.