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Structural, thermal and antifungal activity studies of isomeric Sm(III) Juglonates

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ABSTRACT

Sm(III) chelates of lawsone(LW: 2 hydroxy 1,4 naphthoquinone), juglone(JU: 5 hydroxy 1,4 naphthoquinone), phthiocol(PH: 2 hydroxy, 3 methyl 1,4 naphthoquinone) and plumbagin(PL: 5 hydroxy, 2 methyl 1,4 naphthoquinone)which are called as Sm(III)juglonates, are studied by using Far IR, XRD and SEM. Kinetic parameters of the chelates are reported by using Coats and Redfern equation. Antifungal activity of the chelates against S. Cerevisiae, A. Flavus and C. Albicans is studied and the results are compared within isomeric pairs of chelates.

Key words: Sm(III), Juglones, Kinetic parameters, Antifungal activity.

INTRODUCTION

Samarium complexes have shown a number of applications in various fields like NMR shift reagents[1], luminescent sensors in biological field[2] ,as catalysts[3], antibacterial[4] and anticancer agents[5]. Complexes of "juglones" which are basically hydroxy derivatives of 1,4 naphthoquinone are studied by researchers from past fifty years. Lawsone, juglone, phthiocol and plumbagin are important members of juglones. Lawsone is position isomers juglone and phthiocol is position isomer of plumbagin. Due to change in position of –OH group, lawsone and phthiocol form five membered ring chelates while juglone and plumbagin form six membered ring chelates. Fig.1 There are a very few publications on complexes of juglones and allied ligands with lanthanides as compare to d block elements. Binuclear lanthanide complexes of 2,3 dihydroxy 1,4 naphthoquinone are reported by Khandagale *et al*[6]. Thermal and spectral properties of lanthanide complexes of 3 amino-2-hydroxy-1,4-naphthoquinone are studied by Chikate *et al*[7]. Lanthanide(III) complxes of plumbagin and their cytotoxic effects are studied by Chen *et al*[5]. They have studied the interaction of cytotoxic Sm(III) complex of Plumbagin with bovine serum albumin [8]. Sm(III) complexes of lapacol (2hydroxy-3-(3-methyl-2-butenyl)-1,4-naphthoquinone are studied by Sawhney *etal*.[9]. Kelkar *etal* have studied Holmium complexes of juglones[10].

Considering the increasing importance of lanthanide chelates in the field of catalysis[3,11], study of crystallite size, thermal parameters and study of morphology of the particles of Sm(III) chelates is interesting. In our previous communication we have reported spectral studies of Sm(III) juglonates using FTIR, UV and their antibacterial activity[12]. Present communication is the continuation of this study in which we have reported some interesting physical studies of samarium juglonates like Far IR, powder XRD, SEM, kinetic parameters through thermal analysis and antifungal activity of these chelates. Antimicrobial activity of juglones is another important property of juglones and antifungal properties of juglones are studied by several researchers[13-16]. The antibacterial as well as

antifungal activity of Ca(II) and Mg(II) juglonates is reported by Wadekar *etal*[17]. New antifungal agents are always desired and therefore Sm(III) chelates under study are screened against three fungal strains and the activity is compared within isomeric pairs.

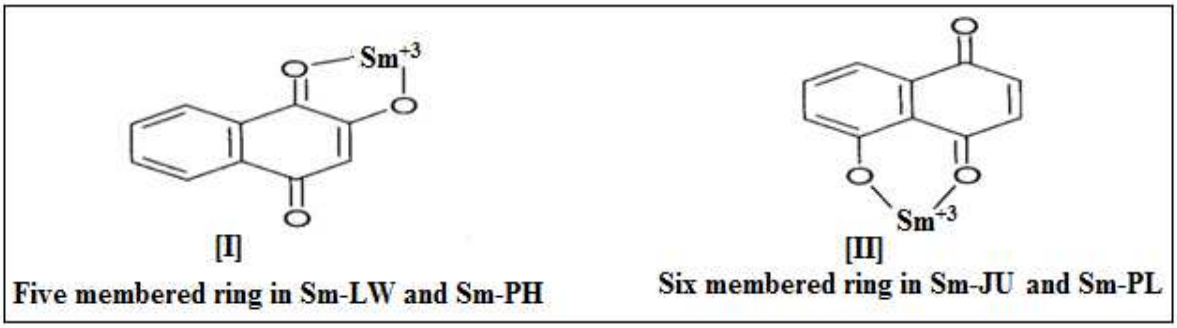


Fig 1. Ring Isomerism in Sm(III) Juglonates

MATERIALS AND METHODS

All chemicals used were of analytical grade. Samarium chloride hexa hydrate was purchased from High Purity Laboratory chemicals, Mumbai. Juglone (5- hydroxyl 1,4- naphthoquinone), Phthiocol((2- hydroxyl, 3 methyl 1,4- naphthoquinone) were prepared by methods reported by Radt[18] and Fisher[19] respectively. The ligands lawsone and plumbagin were purchased from sigma and Hi Media respectively.

Far IR spectra were recorded on Nicolet Model 270, Infrared spectrophotometer in the range 600-50 cm^{-1}. Solution conductivity was measured by using molar solution in DMSO on Systronics conductivity meter 304. Magnetic data at room temperature were collected by using Faraday technique provided with a magneto chemical balance and a permanent magnetic field of 7000 gauss. The thermograms of the chelates were recorded on Shimadzu differential thermal analyzer DTG-60. For the thermal analysis, 3-6 mg sample was used with heating rate of 10^0C per minute, in the temperature range RT to 1000^0C under nitrogen atmosphere. Kinetic parameters were calculated by using computer programme developed by Sarawadekar[20]. The powder XRD was recorded on Bruker D_8 diffractometer, of the diffraction angle (2Ɵ), in the range $(5\text{-}60)^0$. The scanning electron microscopic photographs were recorded on a JEOL-3SM-5200.The antifungal studies of the chelates were done by using well assay method [21].

Synthesis of Chelates:
Methanolic solution of ligands and aqueous solution of metals in 1:3 proportion are mixed and pH is adjusted between 5-6 for lawosonates and phthiocolates and between 6-7 for juglonates and plumbaginates respectively and the mixture was refluxed for 3 hrs. The precipitate of the chelates was filtered and dried under vacuum.

RESULTS AND DISCUSSION

Our previous spectral studies of the chelates indicate that coordination of the ligands with sm(III) is through carbonyl oxygen and hydroxyl oxygen from their decreased values of frequencies in the respective chelates as compared to ligands [17]. The UV-visible studies support the formation of the chelates. The microanalysis and preliminary TG studies confirms the chemical composition of the chelates as $[ML_3.2H_2O]\ nH_2O$.

The Molar conductance and magnetic susceptibility data reported in this communication, supports the chemical composition of the chelates.(Table.1).Some other interesting structural properties of the chelates are also reported here.

Table.1 Physical and Analytical data of Sm(III) juglonates

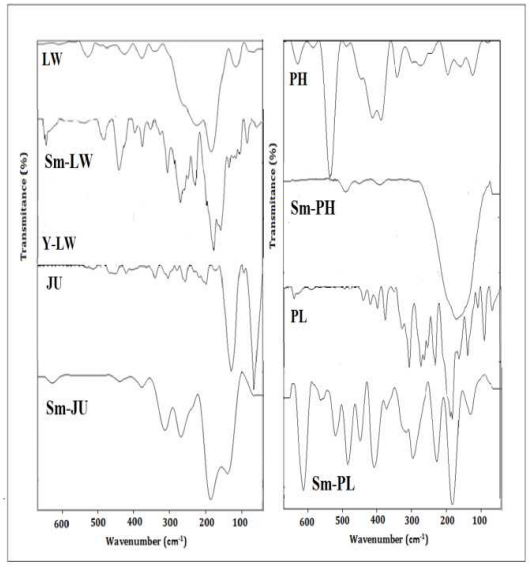
Sr.No.	Compounds	Colour	% Yield	Solubility	Molar Conductance (µs)	Magnetic Susceptibility µ B. M.
1.	DMSO				13.3	----
2.	LW	Yellow	------	DMSO, DMF and Sparingly soluble in water, methanol, ethanol		
3.	Sm-LW	Dark yellow	64.11		0.8	2.34 (1.73)
4.	JU	Orange needle	61.39			
5.	Sm-JU	Dark brown	68.30		1.2	2.53 (1.73)
6.	PH	Yellow	67.53			
7.	Sm-PH	Dark red	82.34		0.9	2.43 (1.73)
8.	PL	Orange	------			
9.	Sm-PL	Deep red	77.75		0.4	2.55 (1.73)

(The values in the parenthesis are theoretical values)

Far IR Studies:

Far IR spectra of metal chelates confirms metal to ligand bonding but Interpretation of Far IR spectra of chelates is always challenging because of possibility of overlapping of M-L bands and the bands of ligands, which are shifted due to chelation with metal [22]. When spectra of free ligands are compared (Fig-2) with spectra of Sm(III) chelates, the nature, peak positions and intensity of the bands is significantly changed. The bands which are either absent in the free ligand or found to be shifted significantly, are given in the Table.2. A peak of medium intensity is observed in all chelates of Sm(III) in the region 613-646 cm^{-1} except in Sm-PH which is absent in respective ligands.

The peaks in the region 308-490 cm^{-1} are assignable to Sm-O bond [23]. Strong bands are observed at 173 cm^{-1} in Sm-LW and Sm-PL. In Sm-JU and Sm-PH, they are observed at 181 and 157 cm^{-1}. The spectra of Sm-PH is notably different than other chelates which contains only three peaks in its spectrum**.**



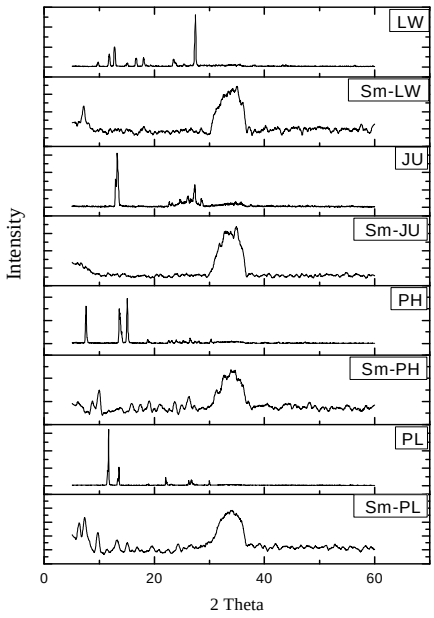


Fig.2 Far IR Spectra of Sm(III) Juglonates. **Fig. 3 XRD Patterns of Sm(III) Juglonates.**

Table.2 FAR IR frequencies in Sm(III) Juglonates (cm^{-1})

Sr. No.	Chelate	IR frequencies in Sm(III) Juglonates(cm^{-1})
1.	Sm-LW	646,636, 482, 268, 248, 225, 173, 154, 79
2.	Sm-JU	633, 434, 308, 263, 236, 181, 137
3.	Sm-PH	488, 385, 157
4.	Sm-PL	613, 404, 290, 219, 173, 121

XRD patterns:

The crystallite sizes of the four ligands, lawsone, juglone, phthiocol, plumbagin and their four chelates with Samarium (III) are determined by using Scherer equation.The XRD patterns are presented in Fig.3 and the crystallite size are summarized in Table 3. The crystallite size of all the eight samples which include the four parent ligands and their four chelates falls in the range of 1.0 to 84.0 nm. Therefore, all these compounds are nanocrystalline in nature.The smallest particle size is shown by Samarium juglonate (1.27 nm) while the largest particle size is shown by ligand plumbagin (83.87 nm).All ligands exhibit their particle size in the range of 15.5 -83.87 nm. After chelation these particle sizes are reduced in the range of 1.27 -15.55 nm. The ligand lawsone shows greater crystallite size than juglone which is almost double. Similarly its Sm(III) lawsonate shows much greater size than its isomeric chelate Sm(III) juglonate. The crystallite size of the ligand plumbagine is more than double than its isomer phthiocol. The same trend is followed by their isomeric chelates also. Therefore in general metal lawsonates and plumbaginates show greater size than corresponding juglonates and phthiocolates. Overall crystallite size reduces as a result of chelation.

Table.3 Crystallite size of Sm(III) juglonates

Sample Code	FWHM	Angle ɵ	Crystallite Size in nm
LW	0.24132	27.44819	33.90194
Sm-LW	0.512	7.1512	15.552
JU	0.51619	13.5174	15.5
Sm-JU	6.53825	33.74442	1.270254
PH	0.23407	15.08091	34.24973
Sm-PH	5.74155	33.92098	1.447194
PL	0.09525	11.67803	83.87337
Sm-PL	4.77317	33.81179	1.740295

SEM studies:

The SEM photographs of the ligands and their chelates are recorded at three magnifications 3,000, 10,000 and 30,000 showing morphological changes as a result of chelation (Fig.4).

In general lawsone shows bulk mass in cubical form which is covered by flappy clusters. Samarium Lawsonate shows micro particles bound together in flowery cluster. Closer view indicates micro particles are bound together in cluster with 95 % boundary merger. Effect of chelation is clearly seen on the morphology. Morphology of juglone is significantly different than lawsone. Morphology of juglone shows fibroid mass forming a fragile network.Samarium Juglonate forms a dense cluster matrix with merged boundries with uniform particle size distribution with partially demarked grain boundaries.

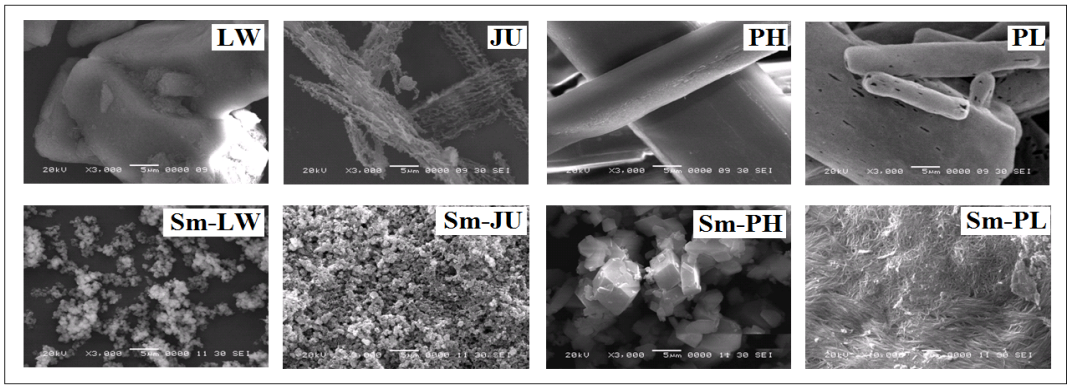


Fig.4 SEM Photographs of Isomeric Sm(III) Juglonates

Ligand phthiocol shows a long smooth rod like structure. Its surface is covered with sparingly occurring granules. Samarium phthiocolates at 10000 magnification of these samples shows rectangular platelet structures with submicron thickness.

Ligand plumbagin shows long rod like structure showing holes on its surface. Length of rods of plumbagin is less as compared to that of phthiocol.They show a network of fine capillary structures woven together and the diameter of capillary is in the submicron range.Distinct change in shape and size of the particles is seen as a result of chelation. When isomeric pairs are compared they also exhibit difference in their morphology. Phthiocolates shows rectangular platelet structure and plumbaginates shows fine capillary like structure.

Effect of methyl substitution also affects the morphology of chelates. Due to presence of methyl group, particles become bigger and square shaped in Sm(III) phthiocolates as compare to corresponding lawsonates. Similarly Sm(III) chelates of juglone and plumbagin shows different morphology from each other.

Thermogravimetry:

The TG curves of the Sm (III) juglonates are illustrated in Fig.5-8 and their stepwise decomposition is given in Table.4 . The kinetic parameters for the step where the significant weight loss is observed, are calculated and given in the Table.5.The coats and Redfern mehod[24] has been employed for the estimation of these parameters and the calculations are done by using computer programmed developed by Sarawadekar[20].

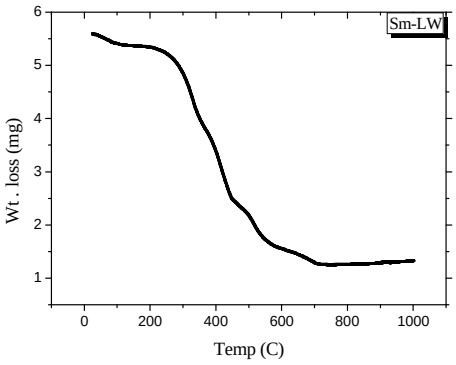


Fig. 5 Thermogravimetry of Sm-LW

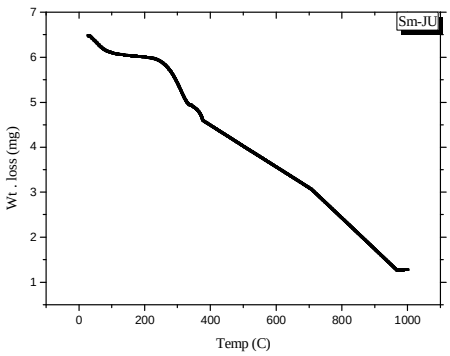


Fig. 6 Thermogravimetry of Sm-JU

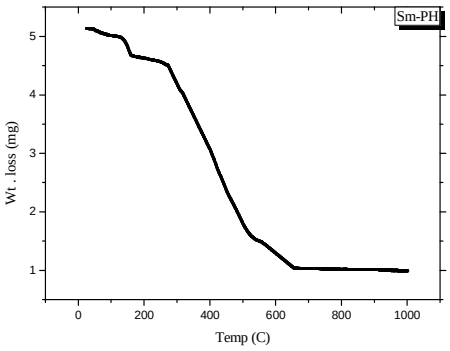


Fig. 7 Thermogravimetry of Sm-PH

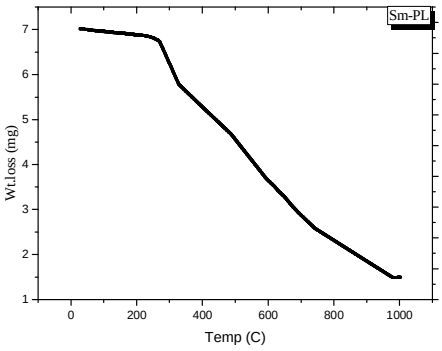


Fig.8 Thermogravimetry of Sm-PL

All the chelates exhibit three or four stages decomposition patterns in the temperature range from room temperature to 982^0C. In the first stage of decomposition which covers the temperature range, room temperature to 100^0C, water associated with these chelates in the form of lattice water or adsorbed water, is lost[25]. In the second as well as third step 100^0C to 450^0C, water associated with these chelates in the form of coordinated water along with the partial decomposition of the one or two ligands takes place. The decomposition observed in the third or fourth stage, covering the temperature range 450^0C to 982^0C, is attributable to the complete decomposition of the second ligand and third ligand along with the partial decomposition of the third ligand.

Table.4 Stepwise Thermal Decomposition of isomeric juglonates of Sm(III)

Sr.No.	Chelates	Stage of Decomposition	Temp. range ˚c	Weight loss in mg.	Weight loss in %	Tentative Assignment
1.	Sm-LW Initial wt=5.59 mg	Ist Stage	25.91-121.13	0.18	3.02 (2.5)	Loss due to one lattice water molecule.
		IInd Stage	207.91-378.23	1.6	28.80 (28.89)	Decomposition of two coordinated water molecules and one ligand.
		IIIrd Stage	378.23-450.93	1.21	21.61 (23.97)	Decomposition of one ligand.
		IVth Stage	450.93-719.38	1.29	23.07 (23.97)	Decomposition of one ligand to give , **Residue:21.82 %**
2.	Sm-JU Initial wt= 6.49 mg	Ist Stage	30.85-114.71	0.44	7.08 (7.11)	Loss due to three lattice water molecules.
		IInd Stage	221.41-728.47	3.2	49.30 (50.31)	Decomposition of two coordinated water molecules and two ligands.
		IIIrd Stage	728.47-962.42	1..61	24.80 (22.83)	Decomposition of one ligand to give , **Residue: 19.41%**
3.	Sm-PH Initial wt= 5.14 mg	Ist Stage	44.09-105.62	0.13	2.52 (2.35)	Loss due to one lattice water.
		IInd Stage	132.88-162.48	0.29	5.64 (4.70)	Loss due to two coordinated water.
		IIIrd Stage	273.86-537.38	3.00	58.36 (49.19)	Decomposition of two ligands and partial decomposition of third ligand
		IVth Stage	537.38-660.19	0.47	9.14	Decomposition of remaining third ligand to give, **Residue: 19.45%**
4.	Sm-PL Initial wt= 7.02 mg	Ist Stage	28.25-273.86	0.29	4.13 (4.81)	Loss due to two coordinated water.
		IInd Stage	273.86-330.46	1.01	23.53 (25.16)	Partial decomposition of one ligand.
		IIIrd Stage	330.46-982.12	4.32	50.98 (50.52)	Decomposition of two ligands and partial decomposition of one ligand to give, **Residue: 21.36 %**

(The values in the parentheses are theoretical values)

After the decomposition of three ligands, the residue is left behind, which is expected to be metal oxide. It is not possible to throw exact light on the nature of these residues without their chemical analyses but it is quite likely that these residues are samarium oxides as experimental value of the residue from TG curve matches with theoretical value calculated from the stoichiometric formula of the chelate. The absence of steepness or distinct/sharp peaks and more horizontal nature of the TG curves is indicative of the nano crystalline nature of these chelates which has been observed in their XRD investigations. The slow weight loss may be due to polymeric nature through hydrogen bondindg of coordinated water molecules[26].

In the present work the Coats and Redfern method[24] has been employed for estimation of kinetic parameters for thermal degradation of selected step. The value of kinetic parameters are given in Table.5 The activation energy values are in the range of 42.44 to 71.21 KJ/mol. The lower values are indicative of nanocrystalline nature of the solid state samples which is consistent with their crystallite size obtained from XRD investigations. All the values of entropy of activation are negative and are in the range of -229 to -235 J/mol k. The negative values are attributable to more disordered or random solid state structure which again supports their nanocrystalline nature. All free energy values are positive and these are relatively higher falling in the range 177.68 – 203.91 KJ/mol. The positive values indicate slow rate of decomposition reactions which is evident from the nature of TG curves. All the enthalpy values which lie between 34.64 – 66.42 KJ/mol are positive which also support the endothermic nature of the decomposition reactions.

Antifungal Activity:

The antifungal investigations of lawsone, juglone, phthiocol, plumbagin and their chelates with Sm(III) were carried out against three fungal strains, i.e. *Saccharomyces Cerivisae* (Laboratory Sprail), *Asperegillus flavus* (NCIM-1028) and *Candida albicans* (NCIM – 3471).These were obtained from National collection of Industrial Microorganisms division of National Chemical Laboratory, Pune. Metal salt $SmCl_3.6H_2O$ was used for comparative purpose of antimicrobial activities. All the test samples are dissolved in DMSO solvent which was used as control. Well diffusion method was employed for the measurement of the activities. The effect of chelation and effect of ring isomerism is studied in the present work.

Table.5 Kinetic Parameters of isomeric Sm(III) juglonates for selected step

Sr. No.	Compound	Temp Range (°C)	Wt Loss. (mg)	Max Corr. Coeff. (r)	Kinetic Model	Order (n)	Activation Energy (E.) KJ/Mol	Entropy (S.) KJ/Mol K	Free Energy (G.) KJ/Mol	Enthalpy (H.) KJ/Mol
1.	Sm-LW	293.54-353.62	0.96	0.99743	Fn	2	46.68	-233.47	185.84	41.72
2.	Sm-JU	273.56-333.35	0.87	0.98665	D3	0	71.21	-229.64	203.51	66.42
3.	Sm-PH	273.51-333.47	0.79	0.99567	Fn	2	42.44	-234.57	177.68	37.64
4.	Sm-PL	273.39-330.46	0.9	0.98444	Fn	2	57.58	-229.27	189.64	52.79

Fresh cultures of the yeast were taken. Suspension of the yeast was prepared in sterile peptone water. Prepared suspension was aseptically seeded in Sabouraud dextrose agar. Seeded agar was poured in sterile petriplates. After cooling four wells of 8mm diameter were bored in each plate. From given samples 2.5mg/ml dilution was prepared in DMSO. Each well was marked with the sample name and with help of micropipette, 0.1 ml of sample dilution was added in respective well. (0.1 ml of sample dilution correspond to 500 µg. Concentration per well). The yeast plates were incubated at room temperature for 3 to 4 days. After incubation the yeasts which are sensitive are inhibited by the test sample and inhibition zone is developed. The diameters of these inhibition zones were measured in mm. The antifungal activity in the present work is expressed in terms of circular zone inhibition areas (mm^2) calculated from r^2 (where r = radius i.e. 0.5 diameter) which is convenient for comparative purpose.

Antibacterial activity of Sm(III) chelates of lawsone, juglone, phthiocol and plumbagin against some bacterial strains is reported by us [17]. Also studies on Ca(II) and Mg(II) complexes of phthiocol and plumbagin for some antimicrobials are reported.[17]. Joshi *et al* have reported antimicrobial activity some plumbagin chelates [27]. The antifungal activity of lawsone is also reported previously [12-15].

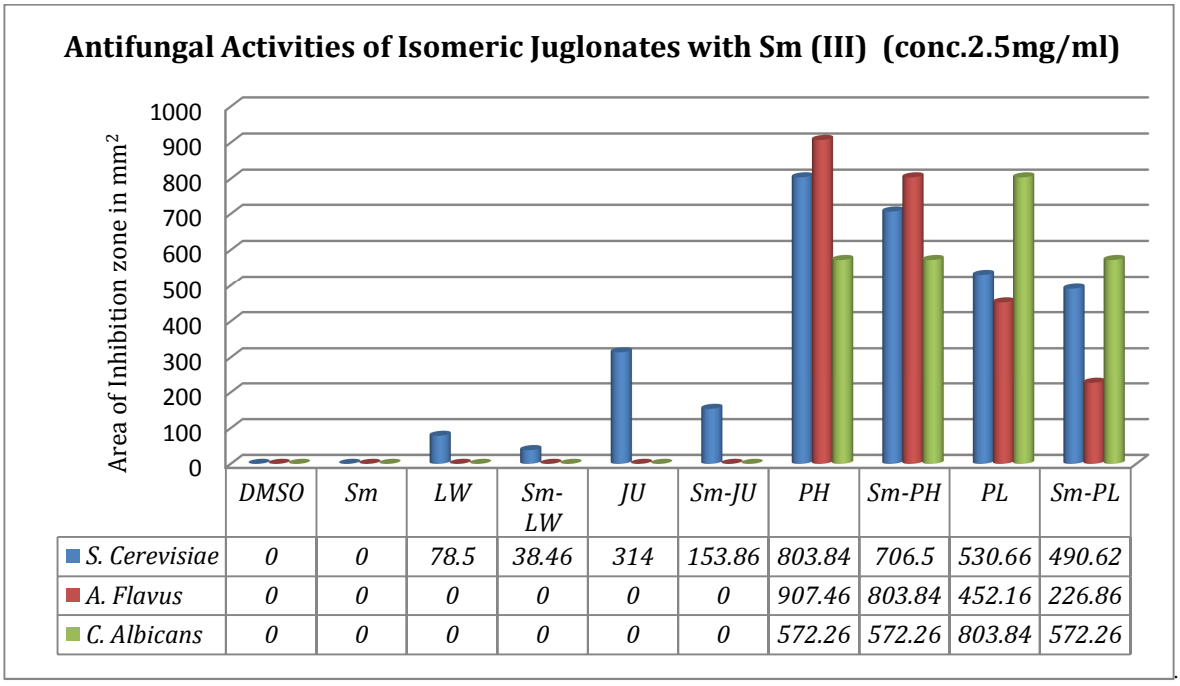
The antifungal activity of all four juglones with their Sm(III) chelates is studied against three fungal strains, *S. Cerevisiae, A. Flavus, C. Albicans* using well assay method and the results are presented in Table.6 and in Fig.9.

The area of inhibition zone is calculated in mm^2 by using the formula πr^2 where r is the radius of inhibition zone. Our method to present the inhibition zone in terms of area instead of diameter is found to be more convenient for comparison of activity of isomeric chelates. The solvent DMSO and salt of Samarium exhibit no activity against the three fungal strains. All the selected ligands and their Sm(III) chelates shows considerable activity against *S. Cerevisiae.* The LW, JU, and their Sm(III) chelates show no activity against *A. Flavus* and *C. Albicans*. On the other hand PH, PL and their chelates show significant activity against all three fungal strains. Therefore effect of methyl group substitution on hydroxyl napthoquinone is notable. In general fungal activity decreases as a result of chelation with Sm(III). Activity Sm-JU is greater than Sm-LW. Activity of Sm-PH is greater than Sm-PL. This exhibits effect of ring isomerism on the activity. Among all the chelates, ligand PH shows highest activity 803.84 mm^2 among the four ligands and same trend is seen after the chelate formation. Sm-PH shows highest activity 706.5 mm^2 among all the chelates.

Table. 6 Inhibition zone of Sm(III) juglonate

Compounds /Chelates	Area of Inhibition zone					
	S. Cerevisiae		*A. Flavus*		*C. Albicans*	
	A mm	B mm^2	A mm	B mm^2	A mm	B mm^2
DMSO	00	00	00	00	00	00
Sm	00	00	00	00	00	00
LW	10	78.5	00	00	00	00
Sm-LW	07	38.46	00	00	00	00
JU	20	314.00	00	00	00	00
Sm-JU	14	153.86	00	00	00	00
PH	32	803.84	34	907.46	27	572.26
Sm-PH	30	706.5	32	803.84	27	572.26
PL	26	530.66	24	452.16	32	803.84
Sm-PL	25	490.62	17	226.86	27	572.26

(Where 'A' is diameter and 'B' is area of the zone)



	DMSO	Sm	LW	Sm-LW	JU	Sm-JU	PH	Sm-PH	PL	Sm-PL
S. Cerevisiae	0	0	78.5	38.46	314	153.86	803.84	706.5	530.66	490.62
A. Flavus	0	0	0	0	0	0	907.46	803.84	452.16	226.86
C. Albicans	0	0	0	0	0	0	572.26	572.26	803.84	572.26

Fig.9 Bar diagram of antifungal activities of Sm(III) juglonates

CONCLUSION

The molar conductance of the Sm(III) juglonates shows non electrolytic nature and magnetic moments give evidence for trivalent oxidation state of the samarium metal present in the chelates. The SEM studies indicate, morphology of Sm(III) juglonates is distinctly different in isomeric pairs The far IR studies of juglonates give evidence for Sm-O bonding. In thermal study, stepwise decomposition of lattice water, coordinated water molecules and three ligands to give samarium oxide of all Sm(III) juglonates is observed. Presence of two coordinated water molecules along with six oxygens from the ligands thus suggest eight coordination of the Sm(III). The negative values of entropy and the lower values of activation energy are indicative of nanocrystalline nature of the solid state samples which is consistent with their crystallite size obtained from XRD investigations. The positive values of Free Energy, indicate slow rate of decomposition which is evident from the nature of TG curves. Also they are indicative of the slowness of the decomposition reactions.The enthalpy values are positive which also support the endothermic nature of the decomposition reactions. In general fungal activity decreases as a result of chelation. In antifungal study, effect of ring isomerism and methyl substitution on naphthoquinone are notable. The Sm(III) phthiocolate shows highest activity against *A. Flavus* while Sm(III) plumbaginate shows highest activity against *C. Albicans.*

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REFERENCES

[1] S.B. Andrews, J.W.Fallert, J. M.Gilliam And R. J. Barrnett, *Proc. Nat. Acad. Sci. USA*, **1973,** 70, 6, 1814-1818.
[2] E. Brunet, O. Juanes, J.C. Rodriguez-Ubis, *Current chemical biology*, **2007**, 1, 11-39.
[3] G. Xanthopoulou, *Applied Catalysis A: General*, **1999**, 185, 185–192.
[4] N. Kumar, H.K. Pandey and G. Chawla, *International Journal of Engineering Science*, **2013,** 2 ,2, 56-60.
[5] ZF Chen, MX Tan, YC Liu, Y Peng, HH Wang, HG Liu, H. Liang, *J. Inorg Biochem.* **2011,**105, 3 , 426-634.
[6] P. Khandagale, R. C. Chikate, S.B.Joshi, B.A.Kulkarni, *Journal of Alloys and Compounds*, **2005,** 392, 112-119.
[7] R. C. Chikate, H. A. Bajaj, A. S. Kumbhar, V. C. Kolhe, S. B. Padhye, *Thermochimica Acta*, **1995,** 249, 239-248.

[8] M. X.Tan, X. Luo, Y. Gu, G. Lu, *Advanced Materials Research*, **2013**, 634-638, 1380-1383.
[9] B. M. L. Bhatia, S. S. Sawhney,(1981),*Thermochimica Acta*,**1981,** 47, 3, 363-366.
[10] V.D. Kelkar, H.R.Gholap, R.R. Gokhale, M.B. Kulkarni, *Indian journal of chemistry*, **1998,** 37A, 915-917.
[11] D. A. Evans, A. R. Muchi, R. Stuermer, *J.Org.Chem.*,**1993**,58, 5307-5309.
[12] P.V. Shinde, S. Nilakhe, V. P. Shinde, B. A. Kulkarni ,V. R. Sapre, M. P. Wadekar, *IOSR Journal of Applied Chemistry (IOSR-JAC)* e-ISSN: 2278-5736. **2014,** 7, 3, 33-40
[13] NM. Rahmoun, Z .Boucherit-Otmani, K .Boucherit, M. Benabdallah, D .Villemin, N. Choukchou-Braham, *Med Mal Infect* **2012**, 42,270-275.
[14] Maria Do Perpetuo Socorro Borges Carriço Ferreira, Mariana Filomena Do Carmo Cardoso, Fernando De Carvalho Da Silva, Vitor Francisco Ferreira, Emerson Silva Lima And Joao Vicente Braga Souza, *Annals of Clinical Microbiology And Antimicrobials* **2014**, 13:26.
[15] N. C. Tran, M.T.Le, D.N. Nguyen, T.D.Tran, *13rd International electronic conference on synthetic Organic Chemistry*, **2009** (ESCOC-13).
[16] U. Sharma, D. Katoch, S. Sood, N. Kumar, B. Sing, A. Thakur and A. Gulati, *Indian Journal of Chemistry*, **2013,** 52B,1431-1440.
[17] M. P. Wadekar, M. S. Itkar, P. V. Shinde, B. L. Khade, *International journal of chemical sciences*, **2012** ,3,11, 1606-1610.
[18] F. Radt, *Elsevier's encyclopaedia of organic chemistry*, **1952,** Series III,12B (Elsevier, Amsterdam,).
[19] L.F. Fieser, *J. Biol. Chem.*,**1940,** 133, 391-396.
[20] R. G. Sarawadekar and I. B. Gade, *Pyro. Tr*., **2006,** 253.
[21] A.W. Bauer, W.M. Kirby, J.C. Sherris, M. Turck, *Am.J. Clin. Pathol*. **1966**, 45, 4,493–496.
[22] S. P. Perlepes, T. F. Zafiropoulos, J. K. Kouinis, and A. G. Galinos, *Z. Naturforsch*. **1981,** 36b, 697-703.
[23] Chempakam Janardhanan Athira, Yesodharan Sindhu,Mathunni Susamma Sujamol and Kochukittan Mohanan, *J. Serb. Chem. Soc.* **2011,** *76* ,2, 249–261.
[24] A.W. Coats and Redfern, *Nature*, **1964,** 201, 68
[25] R. S. Bottei, C. P. McEachem, *J. Inorg. NuclChem*., **1970**,32,8, 2465-2816.
[26] S.B.Jagtap, R.C. Chikate, O.S.Yemul, R.S.Ghadage and B.A. Kulkarni, *Journal of Thermal of Analysis and Calorimetry*, **2004**, 78, 251-262.
[27] C. R. Joshi, G.S. Jagtap, S.V. Chalgeri, *Indian J. Pharmaceut. Sci*., **1988**, 50, 107-108.