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Spectral and antibacterial studies of isomeric Tb(III) Juglonates

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ABSTRACT

Metal chelates of Tb(III) with lawsone, juglone, phthiocol and plumbagin which are hydroxy derivatives of 1,4 naphthoquinone are prepared. The chemical composition of the chelates is obtained by microanalysis and TGA. The spectroscopic properties are studied with the help of IR, UV-visible spectroscopy. The morphological changes after chelation are studied by SEM photographs. The antibacterial activity of the ligands and chelates is examined against three bacterial strains. The thermal spectral and antibacterial properties are compared within isomeric pairs of chelates.

Keywords: Tb(III) chelates, Juglones, spectroscopic properties, antimicrobial activity

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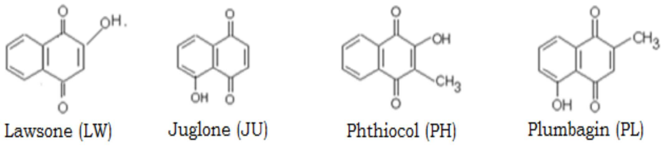
INTRODUCTION

The hydroxyl derivative of 1,4 napthoquinones, constitute a special class of ligands which is known as 'Juglones'. Due to strong chelating ability and versatile nature of these ligands they are studied by various researchers since from last fifty years, from biological, analytical and coordination point of view. Literature review reveals that many transition metal complexes are reported but comparatively less work is reported except a few publications [1-9] on lanthanide chelates of juglones. Now a day's lanthanide complexes are attracting attention due to their number of applications in the fields like luminescent materials [10-11], for biological labeling, in nanochemistry [12], in catalysis [13], as antimicrobial [14] and anticancer agents[15]. Therefore exploration of coordination chemistry of juglones with lanthanide chelates is our current interest. For this purpose four important members of juglones namely lawsone (Fig-1), (I) , Juglone(II), phthiocol(III) and plumbagin(IV) are selected and their chelates with Tb(III) are prepared and studied in present investigation.



Lawsone (LW) Juglone (JU) Phthiocol (PH) Plumbagin (PL)

Fig-1 Parent members of juglone

Fig-2 Ring isomerism in metal chelates of juglones

An interesting aspect of the selected ligands is exhibition of ring isomerism (Fig-2), after chelation. Due to change in position of –OH group on naphthoquinone moity lawsone and phthiocol form five membered ring while juglone and plumbagin form six membered ring with metal ion after chelation. Therefore comparative study of spectral and antimicrobial properties in ring isomeric Tb(III) chelates is another important aspect of the current study.

MATERIALS AND METHODS

Synthesis of ligands

The Lawsone and Plumbagin are commercially available. The Juglone and Phthiocol are prepared by standard procedure, reported by Radt[16] and Fisher[17].

Synthesis of Chelates

The aqueous solution of Lanthanide salt and ligand solution in methanol were taken in the ratio 1:3 proportion and are mixed and refluxed for 45 min at 60° C. Then the pH was adjusted between 5-6 by aq. ammonia solution (10%) and then reaction mixture was refluxed with stirring for 3 hours. After cooling the precipitate was kept in refrigerator and product was filtered and dried in vacuum desiccator.

Instrumental techniques

Chemical characterization of the chelates is done through elemental analysis for percentage of carbon, hydrogen and residue (as metal oxide) by using Thermo Finnigan CHNS and O analyzer and thermo gravimetric analysis was done by Shimadzu model DTG-60 simultaneus DTA-TG apparatus. The morphological study of the ligands and chelates is done with the help of SEM and the photographs are obtained on the microscope JEOL-3SM-5200. The infrared spectra of all ligands and chelates are recorded on Thermo Scientific (Nicolet) spectrophotometer; in the region is 4000-450 cm^{-1}. The solid state electronic spectra of the ligands and their chelates are recorded on U.V-300 double spectrophotometer in the region 200-1100 nm.

RESULTS AND DISCUSSION

The elemental analysis, molecular composition and physical properties of chelate are given in Table-1. They show different visible colours in solid state. The lawsonate and phthiocolates possess deep red or dark red colour and juglone and plumbagin show dark violate coloured chelates.

Table.1: Analytical Data of Tb(III) chelates

Sr. No	Empirical Formula	Color	Yield(%)	Elemental Analysis: Found (Calcd.)		
				C	H	M (as MO)
1.	Tb(LW)32H2O Tb. $C_{30}H_{19}O_{11}$	Deep red	70.23%	50.21% (50.74%)	.06% (3.17%)	22.04% (22.13%)
2.	$Tb(JU)_3 2H_2O$ $Tb.C_{30}H_{19}O_{11}$	Dark violate	65.69%	50.21% (49.97%)	3.06% (2.69%)	22.04% (21.89%)
3.	$Tb(PH)_3.2H_2O$ $Tb .C_{33}H_{25}O_{11}$	Dark red	69.55%	52.18% (52.36%)	3.68% (3.70%)	20.08% (19.86%)
4.	$Tb(PL)_3.2H_2O$ $Tb .C_{33}H_{25}O_{11}$	Dark violate	65.09%	52.18% (52.09%)	3.68% (3.60%)	20.82% (20.60%)

LW: Lawsone JU: Juglone PH: Phthiocol PL: Plumbagin

Thermal study

The number of water molecules and percent residue left after complete decomposition of the chelates was determined by thermo gravimetric study of the chelates[18].The thermal decomposition curves exhibit three to four stage weight loss pattern. In the initial steps, the lattice and coordinated water molecules are lost and then the decomposition of three ligands takes place to give residue. In general the decomposition of Tb(III) juglonates and plumbaninates takes place at higher temperatures than corresponding lawsonates and phthiocolates. This observation indicates that presence of six member ring increases thermal stability of the chelates than five member ring in them.

Infrared spectroscopy

The IR spectra of the ligands and their chelates are shown in Fig-3 and significant IR peaks are summarized in Table-2.

Table-2 Significant IR peaks of Ligands and their Chelates

Sr. No	Compound	ν (OH) cm^{-1}	ν (C=O) cm^{-1}		ν (C-O) cm^{-1}	-CH$_3$ cm^{-1}
			Chelated	Free		
1)	LW	3170	1592	1678	1214	---
2)	Tb-LW	3466	1544	1587	1282	---
3)	JU	---	1643	1664	1225	---
4)	Tb-JU	3419	1594	1633	1290	---
5)	PH	3325	1590	1656	1208	2942
6)	Tb-PH	3561	1539	1621	1232	2918
7)	PL	---	1644	1663	1230	2965
8)	Tb-PL	3447	1610	1638	1253	2964

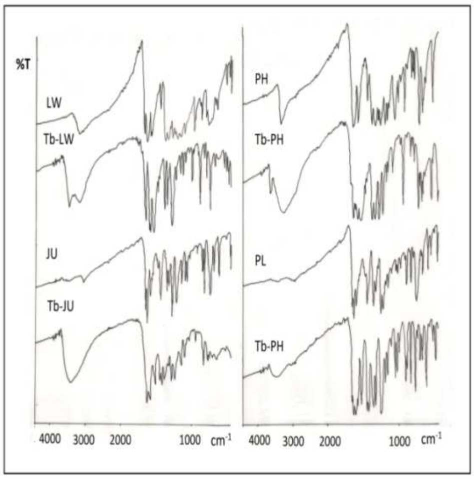


Fig-3 IR Spectra of Ligands and their Chelates

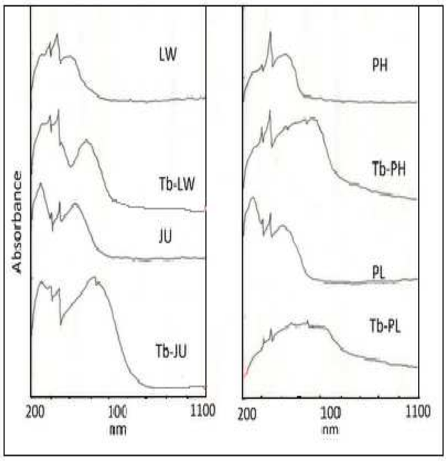


Fig-4 Electronic Spectra of Ligands and their Chelates

OH stretching frequency:

Lawsone shows –OH stretching frequency at 3170cm^{-1} which is absent in its isomer Juglone due to intramolecular hydrogen bonding. As a result of chelation of lawsone with Tb (III), this frequency becomes broad and shifted to longer wavenumber while in case of Tb-JU new broad peak is observed at 3419 cm^{-1}. In both these chelates it is assignable to coordinated or lattice water[19].

Phthiocol shows –OH stretching frequency at 3325cm^{-1} which is absent in its isomer Plumbagin due to involvement of this group in intramolecular hydrogen bonding. As a result of chelation with Tb(III) this frequency becomes broad and shifted to longer wave number while in case of Tb- PL, new broad peak is observed at 3419 cm^{-1}. Here also in both these chelates it is assignable to coordinated or lattice water.

C=O Stretching Frequency:

In all ligands and chelates under study, two C=O groups are present, the first adjacent to OH group may called as chelated C=O while the other is called as free C=O[20,21].The chelated C=O frequency in ligands (1590-1644 cm^{-}

^{1}) is shifted to lower wave numbers after chelation with Tb(III), due to transfer of electron density to metal resulting in weakening of the bond. This indicates that oxygen from chelated C=O is the coordination site. The free C=O frequency is also shifted to lower wave number due to involvement of this bond in chelation indirectly.

C-O Stretching Frequency:

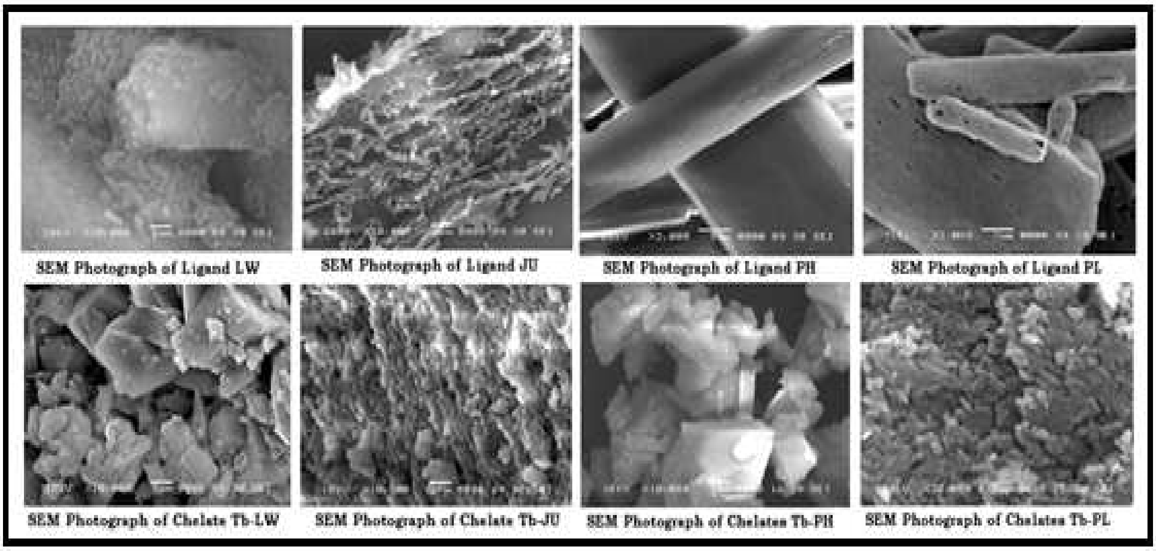
The C-O stretching frequency is directly involved in chelate formation. It is observed in the range of (1208-1230 cm^{-1}). For all chelates it is shifted to higher frequency region showing blue shifts. This indicates C-O bond becomes stronger in chelates than Ligands. This observation is indicative of transfer of electron density from free C=O bond to C-O bond in the chelates.

Electronic Spectroscopy

Table 3:-Absorption maxima of solid state electronic spectra of Ligands and Their Chelates

Sr. No	Compound	Principle band wavelength		
		BET λ nm.	QET λ nm.	n-π*/L→M/ f-f transition λ nm
1)	LW	260	343	394
2)	Tb-LW	264	343	486
3)	JU	247	367	425
4)	Tb-JU	253	343	530
5)	PH	265	352	418
6)	Tb-PH	255	343	558
7)	PL	248	363	407
8)	Tb-PL	306	344	537

In electronic spectra of the ligands, three principal bands are observed, first due to benzenoid electron transfer (BET), second due to quinonide electron transfer (QET), and third due to n-π* [22]. A comparison of spectra of chelates with spectra of their ligands shows that there is a general resemblance between these spectra. Thus spectra of all chelates also consist of three principle bands which are BET, QET and n-π* transition. As a result of chelation there are either red or blue shifts in BET and QET bands observed in all chelates. The third intense band attributed to n-π* transition in all the ligands show a significant change in its position, shape and intensity as a result of chelation. This band becomes broad with a large shift to higher wavelength. In all selected Chelates, the third band is attributable to overlapping of n-π* transitions in the ligands, f-f transitions within the metal and ligand to metal charge transfer in the chelates. The shifting of third band in six membered juglonate and plumbaginate is greater than respective five membered lawsonate and phthiocolate as a result of ring isomerism.



SEM Photograph of Ligand LW

SEM Photograph of Ligand JU

SEM Photograph of Ligand PH

SEM Photograph of Ligand PL

SEM Photograph of Chelate Tb-LW

SEM Photograph of Chelate Tb-JU

SEM Photograph of Chelates Tb-PH

SEM Photograph of Chelates Tb-PL

Fig-5 SEM Photographs of Ligands and Tb(III) Chelates

Scanning Electron Microscopy of Ligands and their Tb(III) Chelates

SEM photographs of ligand and Tb(III) chelates provide valuable information about change in morphology of the ligands as result of chelation. Lawsone show big lumps covered by dusty particles while Juglone shows thin layer one above the other and Phthiocol shows big rod shaped particles while Plumbagin shows porous rod like structure. After chelation, five membered ring chelate, Tb(III) Lawsonate show distorted square shaped particles while six membered ring chelate, Tb(III) Juglonate show agglomeration of small particles with loss of boundaries. After chelation, five membered ring chelate ,Tb(III) Phthiocolate shows square shaped particles while six membered ring chelate, Tb(III) Plumbaginate exhibits short needle shape structure. Distinct change in morphology is a consequence of effect of ring isomerism.

Antimicrobial Activity of Ligands And Chelates

The antimicrobial investigations of Tb(III) chloride, lawsone,juglone, phthiocol, plumbagin and their chelates with Tb(III) are carried out in present investigation using well diffusion method. One Gram negative bacteria i.e *Escherichia coli* (NCIM – 2065) and two Gram positive bacteria which are *Bacillus subtilis*(NCIM – 2063), *Staphylococcus aureus*(NCIM – 2079) were obtained from National collection of Industrial Microorganisms division of National Chemical Laboratory, Pune, for present study. $TbCl_3.6H_2O$ purchased by Aldrich was used for comparative purpose of antimicrobial activities. The antimicrobial activities are studied with special reference to effect of chelation and effect of ring isomerism on the selected compounds.

Each compound was screened against selected bacteria for three concentrations 1mg/ml,1.5mg/ml, 2mg/ml dissolved in DMSO. The activities at these various concentrations are presented in Table-4. The concentration (1.5mg/ml) at which all ligands and all chelates show significant activity are taken for the comparison and the results are shown in Table-5.

Table-4 Antimicrobial activity of Ligands and Tb(III) chelates with Different concentration

Compounds	**Conc. Mg/ml.**	***E. coli***		***B. subtilis***		***S. aureus***	
		A	B	A	B	A	B
DMSO	---	----	----	----	----	-----	----
Tb Cl3.6 H2O	1.0/1.5/2.0	----	----	----	----	----	----
	2.5/3.0/3.5	----	-----	----	----	----	----
LW	1.0	13	132.66	10	78.5	10	78.5
	1.5	18	254.34	11	94.985	12	113.04
	2.0	18	254.34	15	176.62	16	200.96
Tb-LW	1.0	8	50.24	---	---	---	---
	1.5	10	78.5	12	113.04	---	---
	2.0	8	50.24	---	---	---	---
JU	1.0	18	254.34	15	176.62	15	176.625
	1.5	18	254.34	15	176.62	15	176.625
	2.0	18	254.34	16	200.96	15	176.625
Tb-JU	1.0	13	132.66	12	113.04	12	113.04
	1.5	16	200.96	14	153.86	13	132.66
	2.0	16	200.96	14	153.86	14	153.86
PH	1.0	14	153.86	13	132.66	10	78.5
	1.5	16	200.96	13	132.66	11	94.98
	2.0	16	200.96	14	153.86	11	94.98
Tb-PH	1.0	---	---	---	---	8	50.24
	1.5	---	---	10	78.5	9	63.585
	2.0	---	---	11	94.985	8	50.24
PL	1.0	34	907.46	26	530.66	25	490.62
	1.5	36	1017.3	26	530.66	25	490.62
	2.0	36	1017.3	27	572.26	25	490.62
Tb-PL	1.0	24	452.16	14	153.86	16	200.96
	1.5	27	572.265	15	176.625	17	226.865
	2.0	27	572.265	17	226.865	20	314.00

A : Diameter (mm)
B : Area (mm^2)

Experimental Procedure

A suspension of the fresh cultures of the bacteria organisms was prepared in sterile peptone water. This suspension was aseptically seeded in Nutrient Agar for the selected bacterial cultures. The seeded agar was transferred in sterile petriplates. After cooling, four wells of 8 mm diameter were bored in each plate. Each well was marked with the sample name and 0.1 ml of sample dilution was added in respective well with the help of micropipette. Here (0.1 ml of sample dilution correspond to 500 µ g Concentration per well). The bacterial plates were incubated at 37℃ for 48 hrs. After incubation the organisms 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 antimicrobial activity in the present work is expressed in terms of circular zone inhibition areas (mm^2) calculated from πr^2 (where r = radius i.e. 0.5 diameter) which is convenient for comparative purpose as proposed by Kulkarni[6].

RESULTS AND DISCUSSION

Studies on the antibacterial and antifungal properties of 1,4 naphthoquinones and their transition metal complexes are reported previously[23-24].The ligand lawsone, juglone, Phthiocol, and plumbagin exhibit good activity against the selected three microorganisms and the activity of Terbium chloride is zero against all three microorganisms in the present study. A comparison of antimicrobial activity of ligand with their respective chelates shows that all four ligands show grater activity than their Tb(III) chelates. The area of inhibition zone against Gram negative bacteria (*E.Coli*) is greater than Gram positive bacteria (*B.Subtilis, and S.aureus*) for allfour ligands. The ligand Plumbagin show highest antimicrobial activity against all three selected bacteria (Fig-6).The six membered juglone and plumbagin show grater antibacterial activity than lawsone and phthiocol. As an consequence of ring isomerism, six membred chelate Tb-JU show grater activity than five membered ring chelate Tb-LW, against all three microorganism. Similarly, the six membred ring chelate Tb-PL show grater activity than five membred ring chelate, Tb-PH against all three microorganisms. These results are summarized in Table-5 and Fig.-6.

Table-5 Antimicrobial activities of Ligands and their Tb (III) Chelates at Conc. 1.5mg/ml

Compounds	**Circular area of inhibition zone (mm^2)**		
	E. coli	***B. subtilis***	***S. aureus***
DMSO	---	---	---
Tb Cl_3.6 H_2O	---	---	---
LW	254.34	94.985	113.04
Tb-LW	78.5	113.04	---
JU	254.34	176.62	176.625
Tb-JU	200.96	153.86	132.66
PH	200.96	132.66	94.98
Tb-PH	---	78.5	63.585
PL	1017.3	530.66	490.62
Tb-PL	572.265	176.625	226.865

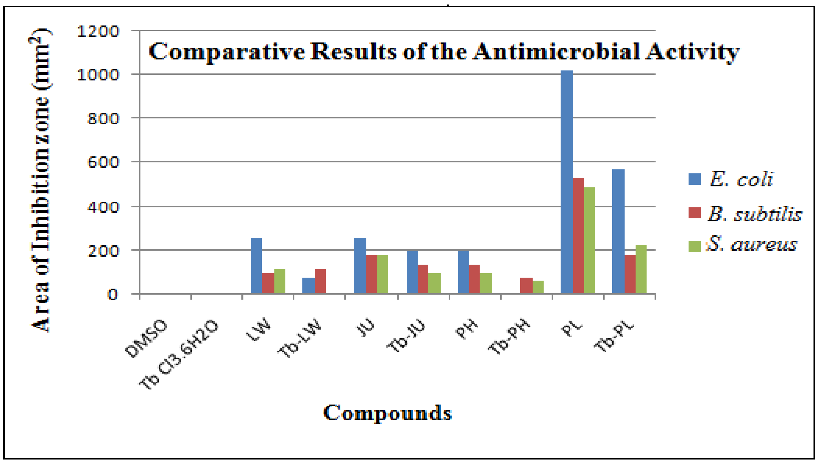


Fig-6 (Bar Digram) Comparison of the Antimicrobial Activity of the Ligands and It's Tb(III) Chelates

CONCLUSION

A Comparative study of spectral and antibacterial properties of Lawsone, Juglone, Phthiocol and Plumbagin is carried out. The I.R. spectral study indicates that six membered chelates of Tb(III) posses stronger metal to ligand bonds as compare to five membered chelates of Tb(III). In electronic spectra large shifting of last band is observed as a result of chelation, indicating combination of metal-ligand charge transfer and f-f transitions in the chelates. The shifting of the third band to longer wavelength is by (92-140 nm). The isomeric pairs of Tb(III) Juglonates show notable difference in their morphology. The antimicrobial activity of Tb-Juglonate and Tb-Plumbaginate is found to be greater than Tb-Lawsonate and Tb-Phthiocolate as a consequence of six and five member ring respectively in isomeric chelates against all three selected microorganisms.

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