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Characterization and Antimicrobial Investigations of Isomeric Pr(III) Juglonates

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Abstract

Hydroxy napthoquinone derivatives constitute an interesting group of ligands which is recognized as 'Juglones'. Isomeric Lawsone-Juglone and Phthiocol-Plumbagin are the most important members of the Juglone series and are biologically active, having natural origin. They form isomeric pairs of ligands resulting into isomeric pairs of metal chelates. The isomerism is occurring due to formation of either five or six membered rings in the metal chelates. In the present work Prasodymium chelates of some isomeric Juglones, namely Pr(III)lawsonate and Pr(III)juglonate, Pr(III)phthiocolate and Pr(III)plumbaginate are synthesized and studied using elemental analysis, UV IR spectroscopy, TGA, XRD and SEM. Antimicrobial activity of the Pr(III) chelates are studied against four bacterial strains. The data and results are employed for investigating structural and antimicrobial properties with particular emphasis on the 'effect of chelation' and 'effect of ring size' on the properties of the chelates. All Pr(III) juglonates are eight coordination chelates. The chelation is through six oxygen from the juglones and through two oxygen from two water molecules. The IR study reveals that, six membered juglone and plumbagin chelates seems to be more stable than five membered lawsone and phthiocol chelates. Effect of ring isomerism is reflected on the antibacterial activity of isomeric chelates showing greater activity in six members juglonate and less activity in plumbaginate for selected bacterial strains. Amoung all chelates Pr(III) plumbaginate exbits highest activity against s.aureius.

Keywords: Hydroxynapthoquinones, Juglones, Pr(III) chelates, IR, Antimicrobial activity

INTRODUCTION

Hydroxy1,4naphthoquinones constitute a class of ligands which are collectively known as 'Juglones'. Lawsone(LW),Juglone(JU),Phthiocol(PH) and Plumbagin(PL)are important members of 'Juglones'(Figure 1). They are bidentate ligands and have two adjacent oxygen atoms per ligand through which they can undergo chelation to form five or six member rings with metals. The metal chelates of juglones are recognized as 'juglonates'. Among the many members of juglones, lawsone and phthiocol form 'five membered' ring and juglone and plumbagin form 'six membered' rings with metals. (Figure 2.). Therefore, they form isomeric pairs of chelates showing significant difference on physical, chemical and biological properties. Exploration of ring isomeric metal chelates is main interest of current research. Previously we have reported spectral and biological studies on some lanthanide chelates of Samarium, Erbium, Terbium and Neodymium [1–4]. In this communication we are reporting characterization and antimicrobial studies on Pr(III) isomeric chelates. Pr(III)lawsonate(Pr-LW) and phthiocolate (Pr-PH) are said to be 'ring isomers' of Pr(III) juglonate (Pr-JU) and plumbaginate(Pr-PL) respectively.

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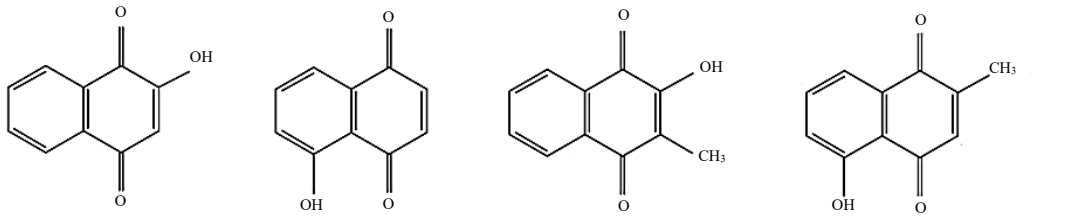
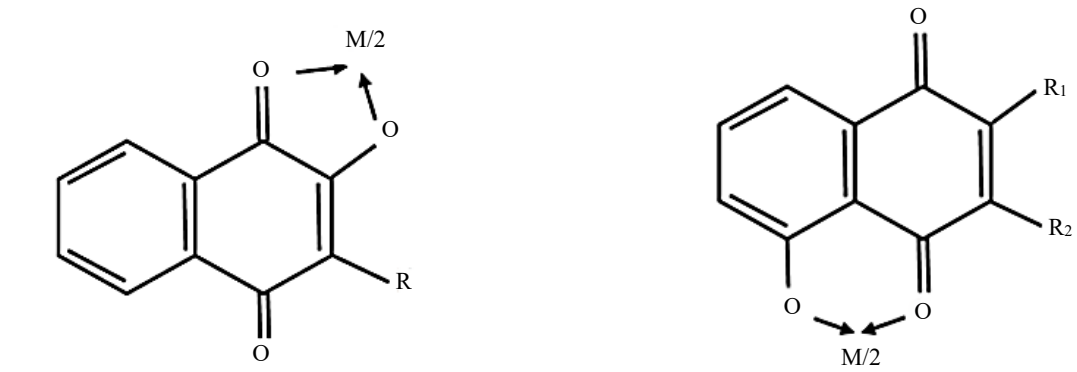


Figure 1. Important members of 1,4 hydroxy naphthoquinones i.e Juglones.



Five mebered Pr(III)LW and Pr(III) PH Six mebered Pr(III)PH and Pr(III) PL

Figure 2. Ring Isomerism in Metal Juglonates.

Lanthanides are gaining importance due to their applications as luminescent labels for bioimaging,MRI contrast agents,in light emmiting diaods and in catalysis [5–8]. Comparatively biological applications of lanthanides are less explored. As most of the juglones exhibit excellent antimicrobial properties [9–12], it is interesting to study the effect of chelation and effect of ring size on the antimicrobial properties of their metal chelates.A comparative study of ring isomeric chelates of Pr(III) will be a novel addition in the coordination chemistry of lanthanides.

MATERIALS AND METHODS

- *Synthesis of Ligands:* The ligand Lawsone and Plumbagin were purchased from Aldrich and Hi media respectively. The Juglone and Phthiocol were prepared by using standard procedures reported in literature [13, 14].
- *Metal Salt:* The metal salt, $PrCl_3$.6H2O was purchased from Aldrich.
- *Synthesis of Chelates:* The chelate precipitates were synthesized by refluxing a methanolic solution of the ligand with an aqueous solution of the $PrCl_3$.6H2O in a molar ratio of 3:1 (ligand: metal) at 65 °C for 30 minutes. To this reaction mixture, a 10% aqueous ammonia solution was added drop by drop to adjust the pH to 5–6. Refluxing was then continued for an additional 2.5 hours to ensure the complete precipitation of the chelates. The resulting precipitates were allowed to cool to room temperature and were stored in a refrigerator for 12 hours to enhance crystallization. The precipitates were then filtered, washed, and dried for further analysis.

Analytical Techniques Used for Characterization

Elemental analysis (C, H and O) of the four juglones and their corresponding Pr(III) chelates was performed using a Thermo Finnigan CHO analyzer. Infrared (IR) spectra were recorded in the range of 4000–450 cm^{-1} using a Thermo Scientific (Nicolet) spectrophotometer. The samples were prepared by homogeneously mixing 1 mg of the compound with 100 mg of dry KBr and then pressing the mixture into transparent pellets. Far-infrared spectra of the juglone ligands and Pr(III) chelates were recorded in the range of 700–50 cm^{-1} using a Nicolet Model 270 spectrophotometer equipped with a Far-IR assembly, to confirm metal-ligand bonding. Thermogravimetric analysis (TGA) and differential

thermal analysis (DTA) of the chelates were conducted using a Shimadzu DTG-60 simultaneous DTA-TG apparatus. Approximately 3–8 g of powdered sample was heated at a constant rate of 10 °C per minute under a nitrogen atmosphere over a temperature range from RT to 1000 °C. The Surface morphology and particle size analysis of the metal chelates were performed using a JEOL JSM-5200 scanning electron microscope (SEM) at magnifications of 3000X, 10,000X, and 30,000X.

Well Diffusion Method for Antimicrobial Activity

The ligands; lawsone, juglone, phthiocol and plumbagin and their Pr(III)juglonates are screened against four bacterial strains which are *B. subtilis, S. aureus, E. coli and P. Aeruginosa* using well diffusion method. The standard procedure was followed as discussed in our previous publication [1-4]. The antimicrobial strains were obtained from National collection of Industrial Microorganisms (NCIM), Division of National Chemical Laboratory, Pune. The metal salt i.e. $PrCl_3.6H_2O$ was purchased by Aldrich, was also screened against the microbes for comparative purpose. The concentration of each of the compound screened was 1.5mg/ml in DMSO.

RESULT AND DISCUSSION

Elemental Analysis

From percent C, H and O, the exact chemical composition of the chelates was determined which is found out to be $[ML_3.2H_2O].nH_2O$.Here M: Metal, L: Ligand, n= one or two lattice water molecules. The composition suggests that, three ligands are coordinating to central praseodymium ion along with two water molecules. Therefore all complexes under study are eight coordinated complexes. The details of elemental analysis is depicted in (Table-1).

Table 1. Elemental Analysis of Pr(III) Juglonates.

Compound	Empirical formula	% C	%H	%O	% Metal
LW	$C_{10}H_6O_3$	68.17 (68.96)	3.77 (3.47)	27.46 (27.56)	-
Pr-LW	$C_{30}H_{19}O_{11}$	50.31 (51.73)	2.29 (2.73)	24.17 (25.29)	19.87 (20.24)
JU	$C_{10}H_6O_3$	71.09 (69.96)	3.23 (3.47)	27.86 (27.56)	-
Pr-JU	$C_{30}H_{19}O_{11}$	47.09 (51.73)	2.54(2.73)	25.02 (25.29)	20.05 (20.24)
PH	$C_{11}H_8O_3$	73.26 (70.20)	4.30 (4.28)	25.55 (25.50)	-
Pr-PH	$C_{33}H_{25}O_{11}$	50.70 (53.66)	3.21 (3.38)	23.40 (23.85)	19.01 (19.09)
PL	$C_{11}H_8O_3$	70.87 (70.20)	4.74 (4.28)	25.01 (25.50)	-
Pr-PL	$C_{33}H_{25}O_{11}$	55.65 (54.06)	2.61 (3.38)	23.17 (23.85)	18.63 (19.09)

Values in the parenthesis indicate theoretically calculated values

Infrared Spectra of Pr(III) Juglonates

The infrared spectra of the four ligands and their corresponding Pr(III) chelates are presented in Figure 3, and the significant absorption bands are listed in (Table 2). The IR spectra of ligands LW and PH, show characteristic hydroxyl stretching vibrations at 3170 cm^{-1} and 3335 cm^{-1}, respectively [15]. In both ligands, the –OH group is located adjacent to the carbonyl group at the C-1 position, which facilitates free hydroxyl vibrations observable in the IR spectra.In contrast, the other two ligands,JU and PL, have the hydroxyl group adjacent to the carbonyl group at the C-5 position. In these molecules, the –OH group is involved in strong intramolecular hydrogen bonding, resulting in the suppression or significant broadening of the hydroxyl stretching band. As a result, no prominent –OH stretching peak is observed in the spectra of these ligands. After chelation with Pr(III), broad absorption bands appear in the 3400–3200 cm^{-1} region for all Pr(III) juglonates. These bands are assigned to the stretching vibrations of –OH groups from coordinated water molecules, confirming the presence of water molecules as the ligands in the coordination sphere of the metal complexes [15].

The carbonyl frequency of each ligand is important as it is involved in the chelate formation. In the selected ligands, C=O frequencies are of two different types. The C=O which will further involve in the chelate formation is named as ‘Chelated C=O’ and the one which remain free is named as ‘Free C=O’[16].

As a result of chelation, both chelated and free C=O frequencies are shifted to lower frequency region due to weakening of the bonds. Weakening of chelated C=O bond indicates that oxygen in this bond is the donor site for coordinating the Pr(III) ion. The free C=O bond is also weakened due to its indirect involvement in the chelate formation. The C-O bond is another bond which is involved in chelate formation which show shift towards higher wave numbers. Simultaneous weakening of free C=O and Strengthening of C-O may indicate withdrawal of electron density from free C=O to C-O. This observation is in agreement with previous reports [1–4,16]. The involvement of phenolic oxygen to coordinates the metal ion during chelate formation is supported by this observation. Therefore IR confirms chelate formation through carbonyl oxygen and phenolic oxygen (Figure 2). The higher values of C=O and C-O frequencies in six membered Pr(III) chelates of juglone and plumbagin than corresponding five member Pr(III) chelates of lawsone and phthiocol indicates stronger bond formation in first two chelates.

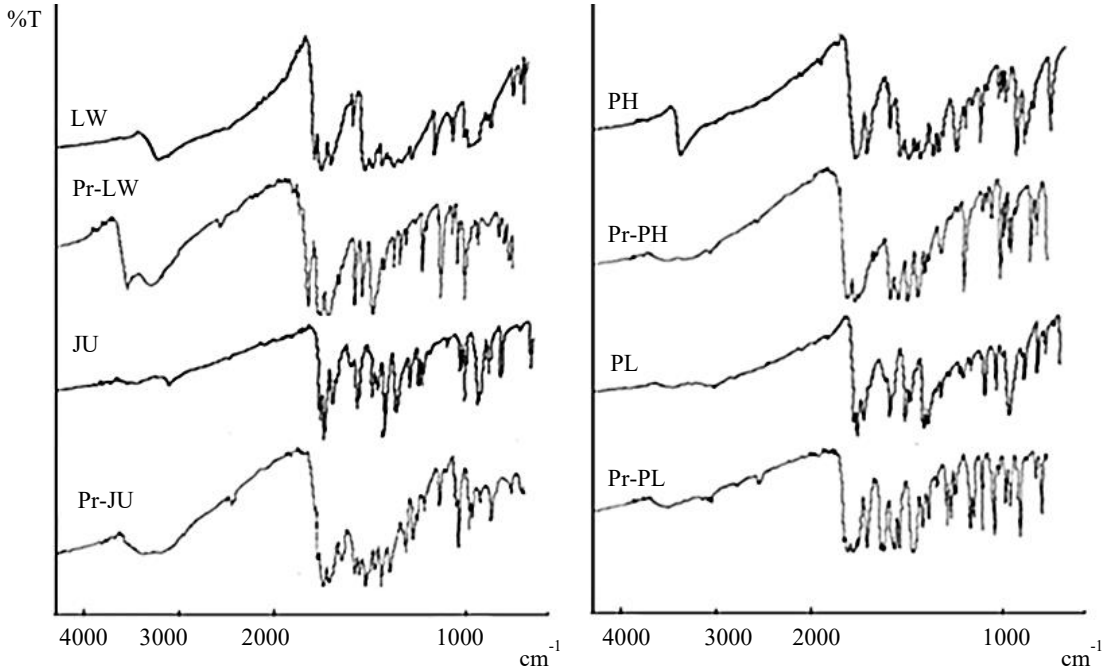


Figure 3. Infrared Spectra of Juglones and Pr(III) Juglonates.

Table 2. Significant IR Frequencies of Pr(III) Juglonates.

S.N.	Compound	ν (OH)(cm^{-1})	ν (C=O) (cm^{-1})		ν (C-O) (cm^{-1})
			Chelated	*Free*	
1)	LW	3170	1578	1678	1214
2)	Pr-LW	3445	1538	1587	1280
3)	JU	-	1643	1664	1225
4)	Pr-JU	3382	1597	1632	1287
5)	PH	3335	1590	1656	1208
6)	Pr-PH	3447	1563	1586	1221
7)	PL	-	1644	1663	1230
8)	Pr-PL	3359	1586	1645	1232

Far IR Spectra

All four ligands under study show no notable peak in the region 300-500cm-1which is the most important region for metal to ligand bonding especially for lanthanide chelates [17]. New strong peaks are arrived in this region at 402, 476-418, 453, 482 & 402 for Pr-LW, Pr-JU, Pr-PH and Pr-PL respectively. These peaks are attributable to Pr-O bonds. Therefore far IR spectra provide strong evidence for metal-oxygen bonds in the Praseodymium chelates.

Thermo Gravimetric Analysis

Thermogravimetric analysis of the metal chelates indicates that the initial weight loss (5-6 %) in the temperature range RT to150^{0}C, corresponds to two water molecules and confirms the presence of coordinated water molecules in the complex [18]. Further chelates are decomposed in three steps to form corresponding metal oxide as residue. Thus TG analysis confirms eight coordination in the Pr(III) juglonates.

SEM Studies

SEM analysis highlights morphological alterations in the ligands upon chelation, as evident from the comparison with their corresponding chelates. (Figure 4). The ligand lawsone shows big lumps covered by dusty particles which after chelation transforms to square shaped particles with definite boundaries and cut corners. The layered structured Juglone changes to granular particles with merged boundaries after formation of Pr(III) juglonate. The Rod shaped particles of phthiocol alters to flowery structure in Pr(III) phthiocolate. Porous rods of ligand plumbagin are changed to mass of merged needle shaped particles. There is a significant difference in the shape and size of the particles of the isomeric pairs of the Pr(III) juglonates which could be due to difference in their ring size.

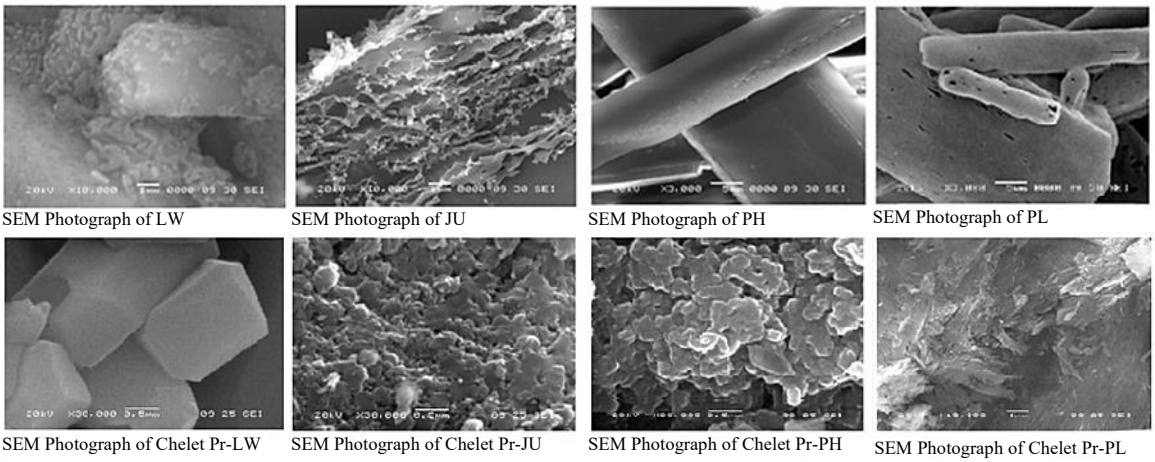


Figure 4. SEM Photographs of Juglones and Pr(III) Juglonates.

Antibacterial Activity of Praseodymium Juglonates

The antibacterial activity of juglones and the praseodymium chelates is carried out against four bacterial strains which are *B. subtilis*, *S. aureus, E. coli* and *P. aeruginosa* using well assay method. The systematic procedure of the method was followed as described in our previous communication [1,16]. The bacterial strains for the present study were obtained from National collection of Industrial Microorganisms division of National Chemical Laboratory, Pune. Metal salt ($PrCl_3.6H_2O$) purchased by Aldrich was used for comparative purpose. All compounds were dissolved in DMSO and the concentration was 1.5mg/ml.

The Important Observations from Antibacterial Activity Study are as Follows

The antibacterial activity of the juglones and its Pr(III) chelates is expressed in terms of circular area of inhibition zone (B) by substituting the radius r from diameter(A) of the zone in the formula πr^2. All Pr(III) juglonates are dissolved in DMSO. The solvent DMSO and $PrCl_3.6H_2O$ exhibit no activity against selected bacterial strains. The circular area of inhibition zone (mm^2) are depicted in Table-3 and relative results are expressed as a bar diagram (Figure 5). Antibmicrobial activities of chelates of Sm(III),Tb(III),Er(III) and Nd(III) with juglones, studied before indicates that, the inhibition of microbes varies with change in metals. The ring size of the chelate affects the extent of inhibition. Effect of isomeric chelates on selected gram-Ve and gram +ve bacteria is also found to be different [1–4]. The present investigations on isomeric Pr(III) chelates supports these investigations.

Table 3. Diameter (A) and Circular Area of Inhibition Zone (B) of Pr(III) Juglonates.

S.N.	Compounds	Circular area of inhibition zone (mm^2)							
		E. coli (-)		*P. aeruginosa (-)*		*S. aureus (+)*		*B. subtilis (+)*	
		A	B	A	B	A	B	A	B
1	DMSO	-	-	-	-	-	-	-	-
2	Pr $Cl_3.6\ H_2O$	-	-	-	-	-	-	-	-
3	LW	-	-	-	-	-	-	13	132.66
4	Pr -LW	-	-	12	113.04	-	-	-	-
5	JU	12	113.04	10	78.5	14	153.86	14	153.86
6	Pr -JU	12	113.04	17	226.86	17	226.86	14	153.86
7	PH	10	78.5	-	-	-	-	16	200.96
8	Pr -PH	-	-	18	254.34	15	176.62	-	-
9	PL	-	-	10	78.5	11	94.98	11	94.98
10	Pr -PL	-	-	15	176.62	20	314.00	12	113.04

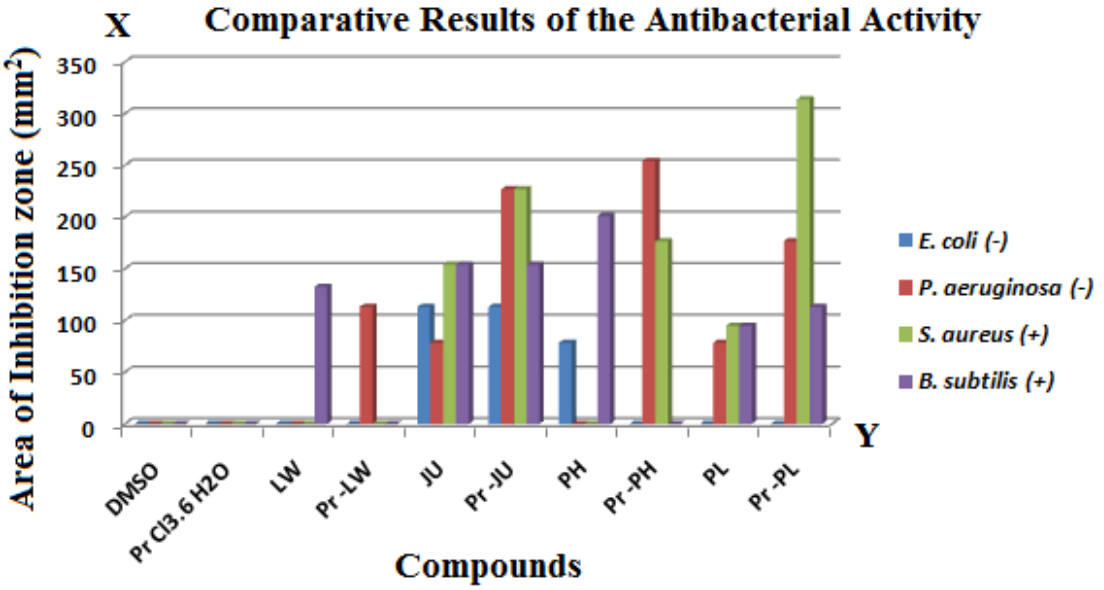


Figure 5. Comparative Results of Antibacterial Activity of Pr(III) Juglonates.

Effect of Chelation

The ligand lawsone show moderate activity only against *B. Subtilius*. Pr(III) lawsonate shows moderate activity against *P. aeruginosa.* The ligand juglone exhibits good activity against all bacterial strains. Pr(III) juglonate show significant activity against all strains and activity against *P. aeruginosa and S. aureus* is notably increased after chelation.

Ligand phthiocol is active against *E Coli and B. Subtilius* and is inactive against *P. aeruginosa and S. aureus.* It is notable that Pr(III)phthiocolate shows good activity against *P. aeruginosa and S. aureus.and activity* against *E Coli and B. Subtilius* is totally lost as a result of chelation. Plumbagin shows moderate activity against *P. aeruginosa, S.aureus* and *B. Subtilius* and no activity against *E Coli*. Pr(III)plumbaginate shows enhanced activity against first three microorganisms and no activity against *E Coli*.Pr(III)plumbaginate shows highest activity against *S. aureus*.

Effect of Ring Isomerism

Lawsone and Juglone are position isomers of each other and demonstrates different ability against antibacterial strains, is clearly seen from the results. Lawsone is active only against one bacterial strain,*B. subtilis* but juglone is active against all bacterial strains. Similar trend is maintained after

chelate formation with Pr(III). Pr(III) lawsonate is active only against *P.aeruginosa.* The antibacterial activity of isomeric Phthiocol and plumbagin is also different from each other. After chelation with Pr(III), phthiocol show greater activity than plumbagin against *P.aeruginosa*. Opposite trend is observed against *S. aureus*. Here Pr(III) plumbaginate exhibits greater activity than corresponding Pr(III) phthiocolate. No inhibition is seen against *B.Subtilius*, by Pr(III) phthiocolate but Pr(III) plumbaginate show moderate activity. Therefore, a noteworthy effect of 'ring size' is observed on antibacterial properties on isomeric pairs of Pr(III) chelates.

CONCLUSIONS

Pr(III) juglonates show eight coordination in their chelates where six oxygen are from ligand juglones and two oxygen are from two water molecules. The IR study reveals that, six membered juglone and plumbaginchelates seems to be more stable than five membered lawsone and phthiocol chelates as seen from the higher values of C=O and C-O frequencies. Morphology of isomeric chelates of Pr(III) is significantly different as examined from SEM photographs. Surface study of Pr(III) chelates could be useful in the field of catalysis. In general Pr(III) juglonates are more active than Pr(III) lawsonates against selected microbes. The trend in inhibition is exactly apposite for isomeric Pr(III) phthiocolate and plumbaginate when activity is compared within corresponding five and six member chelates. Amoung all chelates Pr(III) plumbaginate exhibits highest activity against *s.aureius*.

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