Acta Ciencia Indica, Vol. XLIII C, No. 2, 263 (2017)

SYNTHESIS, SPECTRAL CHARACTERISATION, BIOLOGICAL EVALUATION & CLINICAL SIGNIFICATION OF SOME NEW LANTHANIDE COMPLEXES WITH 2-AZETIDINONES OR B-LACTAMS

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RECEIVED : 13, April 2017

A noble series of Neodymium (III) and samarium (III) complexes of type [Ln(Lac)$_3$Cl$_3$] (Lac = β-lactam or 2-azetidinones; Ln = Nd(III) or Sm(III) have been synthesized and characterized on the basis of elemental analyses, conductance, magnetic moment and spectral (electronic and infrared) data. The thermal behaviour of these complexes has also been studied by TGA and DTA techniques. The antifungal and antiviral activities of the ligands and the complexes were also investigated.

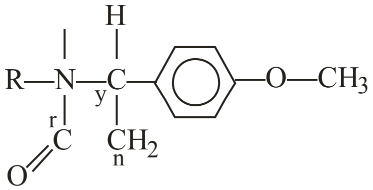
KEYWORDS : Synthesis, lanthanide complexes, anti-bacterial studies, anti-fungal studies.

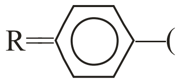
INTRODUCTION

In recent years, a great deal of attention has been given to the study of coordination compounds of lactams [1-9]. These are of interest not only from the theoritical point of view, but also because of their analytical applications, utilization for purification of the lactams and their possible use as modifying or catalysing polymerization agents [8, 10]. Complexes of lactams also play an important role in biological processes and also find applications in pharmacological preparations [1-16] and as effective paint protecting agents [1].

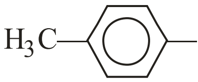
However, very few reports are available on lanthanide complexes of lactams and particularly no study has been done with β-lactams. Moller and coworkers reported 11 some lanthanide complexes with N, N-dimethylformanide. Miller and Madan [6] have prepared lanthanide complexes with γ-butyro lactam and N-methyl-γ-butyro-lactam.

In this paper, we report the synthesis and characterization of neodymium (III) and samarium (III) complexes with β-lactams. The structures of the ligands are shown below –





(Lac$_1$);



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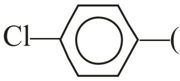
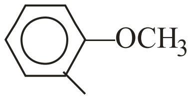
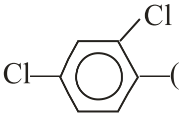


(Lac$_2$);



(Lac$_5$);



(Lac$_3$);

Table 1 : Reactions of neodymium (III) and samarium (III) : chloride with β-lactams or 2-azetidinones.

Reactants	Molar ratio	Refluxing time (hrs.)	Product	Colour	Yield%	Decomp. temp. (°C)
$NdCl_3$+Lac_1	1:3	6	$[Nd(Lac_1)_3Cl_3]$	Green	36	80
$SmCl_3$+Lac_1	1:3	6	$[Sm(Lac_1)_3Cl_3]$	Dark Brown	36	78
$NdCl_3$+Lac_2	1:3	5	$[Nd(Lac_2)_3Cl_3]$	Brown	60	82
$SmCl_3$+Lac_2	1:3	5	$[Sm(Lac_2)_3Cl_3]$	Brown	55	60
$NdCl_3$+Lac_3	1:3	7	$[Nd(Lac_3)_3Cl_3]$	Brown	61	125
$SmCl_3$+Lac_3	1:3	8	$[Sm(Lac_3)_3Cl_3]$	Brown	60	120
$NdCl_3$+Lac_4	1:3	6	$[Nd(Lac_4)_3Cl_3]$	Dark Brown	51	130
$SmCl_3$+Lac_4	1:3	6	$[Sm(Lac_4)_3Cl_3]$	Dark Brown	50	135
$NdCl_3$+Lac_5	1:3	7	$[Nd(Lac_5)_3Cl_3]$	Brown	40	80
$SmCl_3$+Lac_5	1:3	7	$[Sm(Lac_5)_3Cl_3]$	Brown	40	138

where, Lac_1 = 1-phenyl-4(H)-phenyl-2-azetidinone

Lac_2 = 1-O-chlorophenyl-4(H)-phenyl-2-azetidinone

Lac_3 = 1-2, 5-dichlorophenyl-4(H)-phenyl-2-azetidinone

Lac_4 = 1-p-methyl-phenyl-4(H)-phenyl-2-azetidinone

Lac_5 = 1-O-methoxyphenyl- 4(H)-phenyl-2-azetidinone

EXPERIMENTAL

Neodymium (III) and samarium (III) chloride were obtained from BDH and were estimated gravimetrically as oxides. Nitrogen was determined by the Kjeldhal method. Estimations carbon and hydrogen were done in Lucknow. The ligands were prepared by the reported method [12]. The details of the physical measurements are same as described earlier [13].

PREPARATION OF THE COMPLEXES

To a solution of β-lactam (0.03 mole) in absolute ethanol (50 cm^3), was added anhydrous $NdCl_3$ or $SmCl_3$ (0.01 mole). The coloured precipitate was formed which disappeared after few hours of heating the solution. The reaction mixture was refluxed for 6-8 hrs. After filtration, the solvent was distilled off under reduced pressure. The residue was repeatedly washed with ether, to remove excess of β-lactams and dried under reduced pressure at room temperature. The complexes were recrystallized from ethanol

For the sake of brevity, the details of reactions are given in table 1. The analytical data of the reaction products are given in Table 2.

Table 2. Elemental Analyses, Colour and M.P. of the complexes

Complex	Colour	decomp./ temp./C	Found (calcd) %				
			C	H	N	M	Cl
$[Nd(Lac_1)_3Cl_3]$	Green	80	58.6	4.2	4.5	15.5	11.5
			(58.7)	(4.3)	(4.6)	(15.7)	(11.6)
$[Nd(Lac_2)_3Cl_3]$	Brown	82	52.7	3.3	4.0	14.2	21.0
			(52.8)	(3.5)	(4.1)	(14.0)	(20.8)
$[Nd(Lac_3)_3Cl_3]$	Brown	125	52.6	3.2	4.0	14.0	21.0
			(52.9)	(3.3)	(4.1)	(15.1)	(20.8)
$[Nd(Lac_4)_3Cl_3]$	Dark Brown	130	60.0	4.6	4.3	14.9	11.2
			(59.9)	(4.7)	(4.4)	(15.1)	(11.1)
$[Nd(Lac_5)_3Cl_3]$	Brown	80	55.0	4.6	4.2	15.0	10.9
			(55.3)	(4.7)	(4.3)	(14.8)	( )
$[Sm(Lac_1)_3Cl_3]$	Dark Brown	78	58.2	4.0	4.6	16.1	11.6
			(58.3)	(4.2)	(4.5)	(16.2)	(11.5)
$[Sm(Lac_2)_3Cl_3]$	Brown	60	52.0	3.4	4.0	14.2	20.6
			(52.3)	(3.5)	(4.1)	(14.7)	(20.7)
$[Sm(Lac_3)_3Cl_3]$	Brown	120	52.5	3.0	4.0	14.5	20.6
			(52.6)	(3.2)	(4.1)	(14.6)	(20.7)
$[Sm(Lac_4)_3Cl_3]$	Dark Brown	135	59.8	4.6	4.4	15.6	11.8
			(59.9)	(4.7)	(4.3)	(15.5)	(11.9)
$[Sm(Lac_5)_3Cl_3]$	Brown	138	55.0	4.6	4.2	15.0	10.9
			(55.1)	(4.6)	(4.3)	(15.3)	(10.8)

where, Lac_1 = 1-phenyl-4(H)-phenyl-2-azetidinone

Lac_2 = 1-Q-chlorophenyl-4(H)-phenyl-2-azetidinone

Lac_3 = 1-2, 5-dichlorophenyl-4(H)-phenyl-2-azetidinone

Lac_4 = 1-p-methyl-phenyl-4(H)-phenyl-2-azetidinone

Lac_5 = 1-O-methoxyphenyl- 4(H)-phenyl-2-azetidinone

RESULTS AND DISCUSSION

The reactions of β-lactams with $NdCl_3$ or $SmCl_3$ under anhydrous condition result in the formation of following type of complexes:

$$3Lac + LnCl_3 \longrightarrow [Ln(Lac)_3Cl_3]$$

Ln = Nd or Sm

Neodymium (III) and samarium (III) complexes with β-lactams are coloured and amorphous. The elemental analyses (Table-2) clearly show 1:3 (metal to ligand) stoichiometry. The complexes are soluble in ethanol, chloroform, dimethylformamide, dimethylsulphoxide. The complexes are air stable and found to be non-electrolyte in dimethylformamide.

Table 3. Nephelauxetic ratio (β), Covalency parameters (δ) and bonding parameters ($b^{1/2}$) of neodymium (III) and Samarium (III) complexes with β-lactams or 2-acetodopmpmes.

Complexes	β	δ	$b^{1/2}$
$[Nd(Lac_1)_3Cl_3]$	0.9850	1.5228	0.0866
$[Sm(Lac_1)_3Cl_3]$	0.9798	2.0616	0.1005
$[Nd(Lac_2)_3Cl_3]$	0.9852	1.5022	0.0860
$[Sm\ (Lac_2)_3Cl_3]$	0.9800	2.0401	0.0500
$[Nd(Lac_3)_3Cl_3]$	0.9851	1.5125	0.0863
$[Sm\ (Lac_3)_3Cl_3]$	0.0797	2.0721	0.1007
$[Nd(Lac_4)_3Cl_3]$	0.9903	0.9792	0.0696
$[Sm\ (Lac_4)_3Cl_3]$	0.9796	2.0820	0.1010
$[Nd(Lac_5)_3Cl_3]$	0.9861	1.7190	0.0834
$[Sm\ (Lac_5)_3Cl_3]$	0.9800	2.0408	0.0500

Lac_1 = 1-phenyl-4(H)-phenyl-2-azetidinone

Lac_2 = 1-Q-chlorophenyl-4(H)-phenyl-2-azetidinone

Lac_3 = 1-2, 5-dichlorophenyl-4(H)-phenyl-2-azetidinone

Lac_4 = 1-p-methyl-phenyl-4(H)-phenyl-2-azetidinone

Lac_5 = 1-O-methoxyphenyl- 4(H)-phenyl-2-azetidinone

MAGNETIC MOMENT AND ELECTRONIC SPECTRA

Room temperature magnetic moments for neodymium (III) and samarium(III) complexes lie in the range 3.58–3.62 and 1.50–1.54 B.M., respectively. However, the values show little deviation from Van Vleck values [14] *i.e.* 3.68 and 1.93 respectively, and that of hydrated sulphate [15].

Since electrons in the 4f orbitals are well shielded from the ligand field by the intervening $5s^2\ 5p^6$ octet, the order of perturbations for a lanthanide ion is crystal field < spin orbit coupling < interelectronic repulsions. Thus, the line like absorption spectra of the neodymium(III) and samarium(III) chelates arise from electronic transitions within the 4f levels, which are normally forbidden but allowed after the removal of degeneracy in the 4f orbitals by external crystal fields. Neodymium (III) complexes show brands around 11,500–12,000, 12,800–12,900, 13,000–13,200, 13,500–14,000, 18,500-18,700, 19,500,20,000 - 20,800 and 23,000-23,500 cm^{-1} assignable [13] to transitions from the $^4I_{9/2}$ level to the $^4F_{5/2}$, $^2H_{9/2}$, $^4F_{7/2}$, $^2S_{3/2}$, $^4G_{7/2}$, $^2C_{9/2}$, $^4G_{9/2}$, and $^2P_{1/2}$ energy levels, respectively. Samarium (III) complexes show bands around 17,200-17,500, 18,500-18,900, 20,000-20,200, 20,500-20,700, 21,500-22,000, 23,800, 25,000-25,300 cm^{-1} corresponding to the transitions from $^6H_{9/2}$, to $^4F_{3/2}$, $^4G_{7/2}$, $^4I_{13/2}$, $^6P_{5/2}$, and $^4F_{9/2}$, energy levels, respectively.

Nephelauxetic ratio (β), percentage covalency parameter (δ) and bonding parameter ($b^{1/2}$) for neodymium (III) and samarium(III) complexes were calculated using standard procedure [15, 16, 17] and given by following expressions:-

$$\bar{\beta} = \frac{1}{n}\sum_{n=1}^{n} \frac{\nu_{\text{complex}}}{\nu_{\text{aquo.}}}$$

$$\delta = \frac{1-\beta}{\beta} \times 100$$

$$b^{1/2} = \left[\frac{1-\beta}{2}\right]^{1/2}$$

These values find indicate the nature of bonding between metal and ligand is covalent as compared to lanthanide aquo ions and suggest that 4f orbitals are very slightly involved in bonding.

Table 4. Infrared spectral bands (cm^{-1}) of β- lactams and their complexes with neodymium(III) and samarium(III)

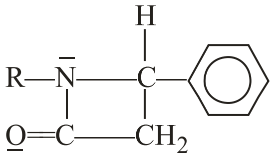
Compound	Data
Lac$_1$	3000m, 2940w, 1690, 1420m, 1340w, 1240m, 1110s, 980w, 820w, 750m,
Lac$_2$	3005m, 2940w, 1700s, 1440w, 1400w, 1340w, 1280m, 1100s, 980m, 800w, 760m,
Lac$_3$	2980m, 1685s, 1520w, 1460m, 1380m, 1250w, 1100s, 1020w, 840m, 750w, 640w,
Lac$_4$	2960mb, 1690s, 1480m, 1460w, 1380m, 1240w, 1110s, 1010w, 980m, 620m
Lac$_5$	3000m, 2940w, 1700s, 1550w, 1460m, 1380m, 1300w, 1240m, 1110s, 960m, 750w, 640m,
[Nd(Lac$_1$)$_3$Cl$_3$]	3000m, 2950w, 1650s, 1430m, 1340w, 1235m, 1130s, 975w, 800w, 760m, 620w, 480m, 300w.
[Nd(Lac$_1$)$_3$Cl$_3$]	2980m, 2960sh, 2920w, 1655s, 1500w, 1420m, 1330w, 1240m, 1120s, 980w, 800m, 720w, 620w, 465m , 310w,
[Nd(Lac$_2$)$_3$Cl$_3$]	3000m, 2950w, 1660s, 1440m, 1410w, 1320m, 1270w, 1120s, 980m, 700m, 640w, 640w, 470m, 320w.
[Nd(Lac$_2$)$_3$Cl$_3$]	2980m, 2940w, 1655s, 1430m, 1400w, 1330w, 1270m, 1120s, 980m, 790w, 640w, 475m, 305w.
[Nd(Lac$_3$)$_3$Cl$_3$]	2980m, 2970sh, 1645s, 1500w, 1450m, 1380m, 1240w, 1120s, 1000s, 820m, 740w, 620w, 480m, 300w
[Nd(Lac$_3$)$_3$Cl$_3$]	2985m, 1635s, 1460m, 1360m, 1240w, 1200w, 1115s, 1010w, 820m, 760w, 620w, 465m, 310w
[Nd(Lac$_4$)$_3$Cl$_3$]	2980m, 2970sh, 1650s, 1500w, 1460m, 1370w, 1250m, 1125s, 1000w, 960m, 720w, 620m, 470m, 320w
[Nd(Lac$_4$)$_3$Cl$_3$]	2980m, 2970sh, 1645s, 1480m, 1360m, 1220w, 1130s, 1010w, 970m, 820m, 640m, 600w, 475m, 315w.
[Nd(Lac$_5$)$_3$Cl$_3$]	3000m, 2920w, 1660w, 1540w, 1460m, 1360m, 1280w, 1240m, 1120s, 1000w, 840m, 620m, 465m, 315w.
[Nd(Lac$_5$)$_3$Cl$_3$]	2960w, 1655s, 1460m, 1400w, 1370m, 1300w, 1240m, 1125s, 950m, 800w, 760w, 620m, 480m, 300w.

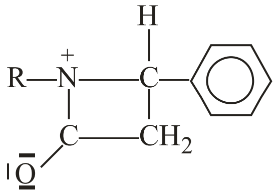
where, Lac$_1$ = 1-phenyl-4(H)-phenyl-2-azetidinone
Lac$_2$ = 1-Q-chlorophenyl-4(H)-phenyl-2-azetidinone
Lac$_3$ = 1-2, 5-dichlorophenyl-4(H)-phenyl-2-azetidinone
Lac$_4$ = 1-p-methyl-phenyl-4(H)-phenyl-2-azetidinone
Lac$_5$ = 1-O-methoxyphenyl- 4(H)-phenyl-2-azetidinone

INFRARED SPECTRA

The infrared spectral bands of ligands and their corresponding complexes are given in Table-4.

The electronic structure of β-lactams may be best described as a resonance hybrid of the following two structures:-





Therefore, β-lactams has two possible centers for coordination, either through oxygen or through nitrogen. The coordination of these ligands to neodymium(III) or samarium(III) has been confirmed by infrared spectra. The infrared spectra of lactams have been studied by several workers [18, 19, 20], new will be added [17, 18, 19, 20] and our conclusions are based on earlier reports.

Table 5. Fungicidal Screening Data

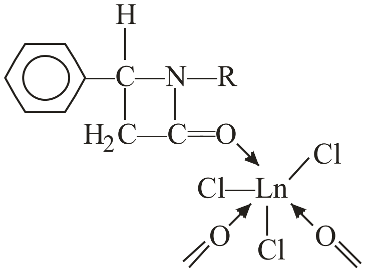
Compound	**Avg. inhibition (%) after 96h.**					
	Organism – A. Niger Concentration			**Organism-H.Oryzae Concentration**		
	1000ppm	**100ppm**	**10ppm**	**1000ppm**	**100ppm**	**10ppm**
Lac$_1$	45.2	40.8	32.6	38.5	35.2	29.8
[Nd(Lac$_1$)$_3$Cl$_3$]	58.4	52.4	50.2	50.8	45.6	40.7
[Sm(Lac$_1$)$_3$Cl$_3$]	60.2	53.2	52.6	56.4	50.2	46.8
Lac$_2$	56.0	48.2	42.8	48.5	40.7	33.6
[Nd(Lac$_2$)$_3$Cl$_3$]	68.4	60.7	56.4	59.8	50.6	42.7
[Sm(Lac$_2$)$_3$Cl$_3$]	72.8	65.4	53.2	64.9	52.3	47.2
Lac$_3$	65.8	52.8	47.3	58.2	47.0	39.6
[Nd(Lac$_3$)$_3$Cl$_3$]	72.4	60.8	54.3	68.0	58.1	42.3
[Sm(Lac$_3$)$_3$Cl$_3$]	76.8	66.2	56.2	69.2	60.4	44.8
Lac$_4$	64.4	50.8	41.6	58.6	40.2	35.4
[Nd(Lac$_4$)$_3$Cl$_3$]	70.2	58.9	46.2	64.2	47.0	42.3
[Sm(Lac$_4$)$_3$Cl$_3$]	72.7	62.1	49.0	66.8	48.2	46.1
Lac$_5$	58.6	49.2	38.4	52.1	42.8	30.7
[Nd(Lac$_5$)$_3$Cl$_3$]	65.4	58.2	444.6	59.1	50.6	40.8
[Sm(Lac$_5$)$_3$Cl$_3$]	68.2	62.6	48.2	60.0	55.1	44.1

where, Lac$_1$ = 1-phenyl-4(H)-phenyl-2-azetidinone
Lac$_2$ = 1-Q-chlorophenyl-4(H)-phenyl-2-azetidinone
Lac$_3$ = 1-2, 5-dichlorophenyl-4(H)-phenyl-2-azetidinone
Lac$_4$ = 1-p-methylphenyl-4(H)-phenyl-2-azetidinone
Lac$_5$ = 1-O-methoxyphenyl- 4(H)-phenyl-2-azetidinone

The infrared spectra of β-lactams, reported in this paper, show one strong band around 1690 cm^{-1} due to υ(C = 0). This band shifts to lower frequency (~40-45 cm^{-1}) in meodymium (III) or samarium(III) complexes. This indicates a decrease of bond order in the C = 0 group as a conseuqnce of the ligand coordination via the donation of lone pairs of electrons at the oxygen atom to the central atom [4, 17, 18]. Further evidence for coordination through the carbonyl oxygen is found by examining the C—N stretching frequency. In the spectra of the ligands, this band is observed at ca 1110 cm^{-1}, which shifts to higher frequency in the complexes (~20-10 cm^{-1}). The decrease in the C = 0 bond that occurs, when result into the metal ion coordinates to the carbonyl oxygen, may the delocolization of the lone pair on nitrogen to the available pπ orbitals of the carbon. This would increase C-N bond border. The υ(Ln-ol) bond is observed at ca 480-465 cm^{-1}. In addition, the far I.R. spectra of the complexes also show bands around 320-300 cm^{-1} assignable to υ(Ln-ol).

Thus, infrared spectral studies indicate that all β-lactams act as neutral, nonodentate ligand coordinating through carbonyl oxygen.

On the basis of available evidences, the following structure may be proposed for neodymium(III) and samarium(III) complexes with β-lactams.



THERMAL STABILITY

The thermal stability, examined by TGA and DTA techniques, is rather complicated for these complexes. The TGA curves show continuous weight loss in the temperature range 185-230°C to 400-445°C. However, at this temperature range, different plateaus could be observed but weight losses do not correspond to formation of definite intermediate products. Kotek and Dusek reported the TGA for Co(III) complexes of 8-caprylolactam and observed the similar behaviour. They assigned different plateaus in TGA curves due to polymerization of non-decomposed lactam, which retards the decomposition and this retardation shows up in TGA curves by the plateaus mentioned. This assumption seems to be correct in our cases also since intermediate products are found to be insoluble in all common organic solvents. Finally, all the compounds decompose to give Ln_2O_3 (Ln-Nd or Sm). The weight loss found is in agreement with the calculated value.

DTA curves show two endothermic peaks at ca 220-230°C and 300-315°C. These endoeffects appear obviously to the polymerization and polymer decomposition.

Finally, DTA curves also show one strong exothermic peak in temperature range 420-450°C, when combustion of organic ligand by means of air oxygen takes place. The final decomposition product, as confirmed by analyses and far I.R. spectra, is Ln_2O_3 (Ln=Nd or Sm).

ANTIFUNGAL ACTIVITY

The fungicidal activity of the complexes was evaluated against Aspergillus niger and Helminthosporium oryzae by agar plate technique [21, 22] at three concentrations: viz, 1000 ppm, 100 ppm, and 10 ppm, with three replications in each case. The average percentage inhibition after 96 hours by various compounds was calculated from the expression below:

$$\text{inhibition (\%)} = 100\ \frac{C-T}{C}$$

C = diameter of fungus colony in control plates after 96h; and T= diameter of fungus colony in tested plates after 96h.

The results are recorded in Table 5. The following conclusions can be derived.

(a) All the compounds have significant toxicity at 1000 ppm against both species of fungi and the complexes are more active than their corresponding lactams. In other words, the activity increase on complexation.

(b) Activity decrease on dilution.

(c) The lactams and their corresponding neodymium(III) and samarium(III) complexes are more active against Aspergillus niger than Helminthosporium oryzae.

Table 6. Antiviral Activity of the complexes

Compound	**Organism-Cucumber mosaic virus Host Plant-Chenipodium amaranticolor Concentration 1000ppm**
	Inhibition %
Lac_1	12
$[Nd(Lac_1)_3Cl_3]$	20
$[Sm(Lac_1)_3Cl_3]$	24
Lac_2	18
$[Nd(Lac_2)_3Cl_3]$	24
$[Sm(Lac_2)_3Cl_3]$	26
Lac_3	25
$[Nd(Lac_3)_3Cl_3]$	28
$[Sm(Lac_3)_3Cl_3]$	30
Lac_4	8
$[Nd(Lac_4)_3Cl_3]$	12
$[Sm(Lac_4)_3Cl_3]$	15
Lac_5	12
$[Nd(Lac_5)_3Cl_3]$	15
$[Sm(Lac_5)_3Cl_3]$	18

where, Lac_1 = 1-phenyl-4(H)-phenyl-2-azetidinone

Lac_2 = 1-Q-chlorophenyl-4(H)-phenyl-2-azetidinone

Lac_3 = 1-2, 5-dichlorophenyl-4(H)-phenyl-2-azetidinone

Lac_4 = 1-p-methylphenyl-4(H)-phenyl-2-azetidinone

Lac_5 = 1-O-methoxyphenyl- 4(H)-phenyl-2-azetidinone

ANTIVIRAL ACTIVITY

The antiviral activity was evaluated by nothing the reduction in number of local lesions produced by cucumber virus on Chenopodium amaranticolor, when mixed with the chemical quantity of solution of lactams and their complexes. Inoculations were made by the leaf rubbing method. One half of each leaf was inoculated with inorculum, containing the virus and chemical, and the remainder was inoculated with the standard virus extract. Infections on different samples were calculated on the basis of local lesions produced by each treatment and percentage inhibition was calculated from the expression below.

$$\%\text{ inhibition} = \frac{\text{No. of Local lesions by control} - \text{No. of lesions by treatment}}{\text{No. of lesions by control}}$$

All compounds display a weak antiviral activity (Table 6). However, the lactams are less active than their corresponding complexes.

ACKNOWLEDGEMENTS

The authors wish to thank the CSIR for the award of the Research Associates ship to S.A.

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