

# Ditolyldithiophosphates of Cerium (III): Synthesis, Spectroscopic and Thermal Characterization and Antimicrobial Screening

Atiya Syed\*<sup>1</sup> and Seema Verma<sup>2</sup>

<sup>1,3</sup>Department of Chemistry, University of Jammu, Jammu, India

<sup>2</sup>Department of Physics, University of Jammu, Jammu, India

## ABSTRACT

Ditolyldithiophosphate complexes of cerium(III) corresponding to  $[(\text{ArO})_2\text{PS}_2]_3\text{Ce}$  (Ar = *o*-, *m*-, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> and *p*-Cl-*m*-CH<sub>3</sub>C<sub>6</sub>H<sub>3</sub>), have been synthesized and characterized by various physico-chemical techniques like elemental analyses, mass, IR, NMR (<sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P) spectral studies. A six coordinated cerium atom has been established in the complexes. The thermogravimetric analysis has been carried out which was consistent with the characteristic decline in weight of dithiophosphate complexes resulting in CeS<sub>2</sub> as the final residue which is formed by oxidation of Ce(III) to Ce(IV). Antimicrobial screening of the complexes against two bacterial strains: Gram-negative, *Klebsiellapneumoniae* and Gram-positive, *Bacillus cereus* and fungus *Penicilliumchrysogenum* have shown potential bioactivity.

**Keywords:** Cerium, Dithiophosphate, Phosphorus, Sulfur, Antimicrobial, TGA

## I. INTRODUCTION

Rare earth elements have been of interest since decades as they have exhibit versatile coordination chemistry and their complexes play an important role in chemical[1], medical,[2] and industrial[3] processes. Cerium is particularly, the most abundant lanthanide and its importance is due to its catalytic behavior[4], application in catalytic converters[5], in flat-screen TVs, low-energy light bulbs and floodlights[6]. The well-developed dithiophosphate chemistry of transition metals, due to their fascinating modes of bonding[7-9] along with increasing applications in industry[10] and agriculture[11] is much extensive. Few reports are available on lanthanides with such ligands and ditolyldithiophosphates of lanthanide and actinide elements and their adducts have received little attention[12-14]. Recently, we have reported ditolyldithiophosphates of lanthanum(III) and their adducts with nitrogen and phosphorus donor bases[15]. In continuation of our research interest in ligands containing phosphorus and sulphur, we thought it

worthwhile to study the ditolyldithiophosphates of cerium(III).

## II. METHODS AND MATERIAL

Stringent precautions were taken to exclude moisture. Moisture was carefully excluded throughout the experimental manipulations by using standard Schlenk's techniques. *Ortho*-, *meta*- and *para*-hydroxytoluene (cresols) were distilled before use. Cerium trichlorideheptahydrate (Himedia) was used as received. The solvents used (toluene, hexane and chloroform) were purified and dried by standard methods before use. The ligands (*o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>PS<sub>2</sub>Na, (*m*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>PS<sub>2</sub>Na, (*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>PS<sub>2</sub>Na and (*p*-Cl-*m*-CH<sub>3</sub>C<sub>6</sub>H<sub>3</sub>O)<sub>2</sub>PS<sub>2</sub>Na were prepared by literature method[16]. Elemental analyses of C, H, N and S were done on Vario EL III and CHNS-932 Leco elemental analyzer their results were found to be in good agreement (±0.3%) with the calculated values. Chlorine was estimated volumetrically by Volhard's method. Cerium was estimated gravimetrically as Cerium oxide (Ce<sub>2</sub>O<sub>3</sub>)[17]. The mass spectra were recorded on

ESQUIRE3000\_00037 spectrophotometer. IR spectra were recorded using KBr pellet in the range of 4000-200  $\text{cm}^{-1}$  on a Perkin Elmer Spectrum 400-I FTIR spectrophotometer. The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were recorded in  $\text{CDCl}_3$  on BrukerAvance II and III 400 (400 MHz) spectrometer using TMS as internal reference for  $^1\text{H}$  and  $^{13}\text{C}$  NMR and  $\text{H}_3\text{PO}_4$  (85%) as external reference for  $^{31}\text{P}$  NMR. The thermogram was analyzed by using Perkin Elmer, diamond TG/DTA instrument. Recrystallized alumina sample holder was used and the heating rate of 10  $^\circ\text{C}$  per minute. The thermogram was recorded in the temperature range from 30  $^\circ\text{C}$  to 1000  $^\circ\text{C}$ . The experiment was carried out under a flow rate of 50 mL per minute of nitrogen atmosphere.

### Synthesis of complexes

#### Synthesis of Tris-*O,O'*-ditolyldithiophosphato - cerium(III) [ $\{(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_3\text{Ce}$ ] (1)

Table 1. Synthetic and analytical data of ditolyldithiophosphates of cerium(III)

S. No.	Reactants g (mmol)		Molar ratio	Reflux time (h)	Product (Physical state)	Yield (%)	Analysis % Found (Calc.)				
	LNa	CeCl <sub>3</sub> .7H <sub>2</sub> O					C	H	S	Cl	Ce
1.	1.00 (3.01)	0.37 (1.00)	3:1	3	[ $\{(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_3\text{Ce}$ ] (White solid)	89	47.18 (47.22)	3.69 (3.96)	17.97 (18.01)	--	13.05 (13.12)
2.	1.00 (3.01)	0.37 (1.00)	3:1	3	[ $\{(m\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_3\text{Ce}$ ] (White solid)	86	47.16 (47.22)	3.78 (3.96)	17.86 (18.01)	--	13.09 (13.12)
3.	1.00 (3.01)	0.37 (1.00)	3:1	3	[ $\{(p\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_3\text{Ce}$ ] (White solid)	90	47.13 (47.22)	3.71 (3.96)	17.81 (18.01)	--	13.07 (13.12)
4.	1.00 (2.49)	0.31 (0.84)	3:1	3	[ $\{(p\text{-Cl-}m\text{-CH}_3\text{C}_6\text{H}_3\text{O})_2\text{PS}_2\}_3\text{Ce}$ ] (White solid)	91	39.49 (39.57)	2.74 (2.85)	14.87 (15.09)	16.58 (16.69)	10.87 (10.99)

LNa = (*o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>PS<sub>2</sub>Na (1), (*m*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>PS<sub>2</sub>Na (2), (*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>PS<sub>2</sub>Na (3), (*p*-Cl-*m*-CH<sub>3</sub>C<sub>6</sub>H<sub>3</sub>O)<sub>2</sub>PS<sub>2</sub>Na (4)

### Antimicrobial Activity

In this procedure [18], agar plates were inoculated with standardized inoculums of the test microorganism (gram-negative, *Klebsiella pneumoniae* and gram-positive, *Bacillus cereus* and fungus *Penicillium chrysogenum*). Then, filter paper discs (about 6mm in diameter), containing the complex at a particular concentration, were placed on the agar surface. Four concentrations (100, 200, 400 and 800 ppm) were made to obtain data of antibacterial activity of complex with varying concentration. The petridishes were incubated under suitable conditions. Antimicrobial complex diffused into the agar and inhibited

A chloroform solution ( $\sim 10 \text{ cm}^3$ ) of cerium trichlorideheptahydrate (0.37 g, 1.00 mmol) was added to a chloroform solution ( $\sim 20 \text{ cm}^3$ ) of sodium *O,O'*-ditolyldithiophosphate (1.0 g, 3.00 mmol) with constant stirring at room temperature for two hours followed by refluxing for five hours; white turbidity appeared due to the formation of sodium chloride. The contents were cooled and then sodium chloride was separated by filtration using alkoxy funnel fitted with G-4 disc. The product [ $\{(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_3\text{Ce}$ ] (1) was obtained as white solid from the filtrate after removal of excess of chloroform in *vacuo*.

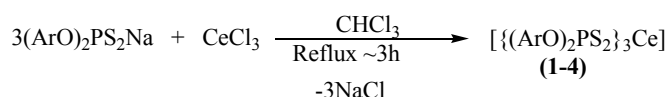
The complexes 2-4 were prepared by the same procedure. The synthetic and analytical details of complexes 1-4 are listed in the Table 1.

germination and growth of the test microorganism and then the diameters of inhibition growth zones were measured. It is pertinent to mention that in case of antibacterial screening Mueller Hinton Agar was used while for carrying out antifungal analysis Potato Dextrose Agar was used.

### III. RESULTS AND DISCUSSION

Dithiophosphates of cerium(III) (1-4) were prepared as white solid in 86-91% yield by the reaction of cerium trichlorideheptahydrate, CeCl<sub>3</sub>.7H<sub>2</sub>O, with sodium salt of *O,O'*-di(*o*-, *m*-, *p*- and *p*-chloro-*m*-tolyl)dithiophosphates, (ArO)<sub>2</sub>PS<sub>2</sub>Na [Ar = *o*-, *m*-, *p*-

CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, *p*-Cl-*m*-CH<sub>3</sub>C<sub>6</sub>H<sub>3</sub>] (**1-4**), in 1:3 molar ratio in chloroform under refluxing condition.



[Ar = *o*-, *m*- or *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> (**1-3**) and *p*-Cl-*m*-CH<sub>3</sub>C<sub>6</sub>H<sub>3</sub> (**4**)]

**Scheme 1:** Synthesis of tris-*O,O'*-di(*o*-, *m*-, *p*- and *p*-chloro-*m*-tolyl)dithiophosphates of cerium(III) (**1-4**).

These complexes were obtained after separation from NaCl. These complexes are soluble in tetrahydrofuran, chloroform, DMSO and insoluble in solvents like *n*-hexane and carbon tetrachloride. These complexes appear to be slightly moisture sensitive.

### IR Spectra

Two strong intensity bands were observed in the IR spectra of these complexes in the region 1253.6-1185.0 cm<sup>-1</sup> and 1016.6-882.8 cm<sup>-1</sup>, have been ascribed to the ν(P)–O–C and νP–O–(C) vibrations, respectively. The observation of two closely spaced bands arising from ν(PS<sub>2</sub>) vibrations bands for νP–S<sub>(asym)</sub> and νP–S<sub>(sym)</sub> in the region 711.7-528.0 cm<sup>-1</sup> and 591.8-456.8 cm<sup>-1</sup> is characteristic of bidentate chelating dithiophosphates units. The presence of a band in the region 381.9-369.1 cm<sup>-1</sup>, attributed to νCe–S, is indicative of the formation of cerium-sulfur bond. This is supported by the literature survey[15-16]. The relevant IR spectral data of these complexes are given in Table 2.

**Table 2** IR spectral data of the dithiophosphates of cerium(III) (in cm<sup>-1</sup>).

S. No.	ν(P)–O–C	νP–O–(C)	νP–S <sub>(asym)</sub>	νP–S <sub>(sym)</sub>	νCe–S
1.	1185.0, s	832.8, s	528.0, s	591.8, m	381.1, w
2.	1211.0, s	1016.6, s	681.1, s	519.5, m	369.1, w
3.	1245.0, s	979.7, s	711.7, s	567.0, m	378.1, w
4.	1253.6, s	916.0, s	598.0, s	456.8, m	379.5, w

s = strong, m= medium, w = weak

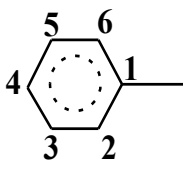
### <sup>1</sup>H NMR Spectra

The <sup>1</sup>H NMR spectral data of all complexes show characteristic chemical shift splitting pattern for tolyl protons which is consistent with the proposed structure. Two resonances were observed for the ring protons of *para* derivative whereas four resonances were observed for *ortho* (**1**) and *meta*. The *p*-chloro-*m*-tolyl derivative shows three signals. No significant changes were observed as a result of being linked to cerium[16]. The chemical shifts of methyl (CH<sub>3</sub>) protons of the tolyl rings were observed as singlet in the region 2.01-2.18 ppm. The aromatic protons of the tolyl rings were observed in the region 6.56-7.26 ppm. Moreover, the coupling constant of multiplets were in agreement with the predicted chemical structure. The relevant <sup>1</sup>H NMR spectral data of these complexes are given in the Table 3.

### <sup>31</sup>P NMR Spectra

The dithiophosphate phosphorus resonated in the region 91.3-93.5 ppm as a singlet in the spectra of these complexes. The observed singlet with a downfield shift in comparison to the parent dithiophosphate ligands is indicative of the symmetrical environment and bidentate mode of linkage of the dithiophosphate ligands with cerium[16,19] <sup>31</sup>P NMR spectra of the complexes have been summarized in Table 3.

**Table 3**  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectral data of the ditolyldithiophosphates of cerium(III) (in ppm).

S. No.	$^1\text{H}$ NMR		$^{31}\text{P}$ NMR
	$-\text{CH}_3$		
1.	2.20, s, 18 H, CH <sub>3</sub>	7.01, d, 6 H <sub>(3)}</sub> ( $J = 7.6$ Hz); 6.71, t, 6 H <sub>(4)}</sub> ( $J = 8.4$ Hz); 7.11, t, 6 H <sub>(5)}</sub> ( $J = 7.4$ Hz); 6.82, d, 6 H <sub>(6)}</sub> ( $J = 8.4$ Hz)	91.8, s
2.	2.04, s, 18 H, CH <sub>3</sub>	6.72, s, 6 H <sub>(2)}</sub> ; 7.01, d, 6 H <sub>(4)}</sub> ( $J = 7.9$ Hz); 7.13, t, 6 H <sub>(5)}</sub> ( $J = 8.1$ Hz); 6.94, d, 6 H <sub>(6)}</sub> ( $J = 8.4$ Hz)	92.3, s
3.	2.17, s, 18 H, CH <sub>3</sub>	7.05, d, 12 H <sub>(2,6)}</sub> ( $J = 8.4$ Hz); 6.78, d, 12 H <sub>(3,5)}</sub> ( $J = 8.4$ Hz)	91.3, s
4.	2.18, s, 18 H, CH <sub>3</sub>	6.66, s, 6 H <sub>(2)}</sub> ; 6.56, d, 6 H <sub>(5)}</sub> ( $J = 8.1$ Hz); 7.08, d, 6 H <sub>(6)}</sub> ( $J = 8.2$ Hz)	93.5, s

s = singlet, d = doublet, t = triplet, m = multiplet

### $^{13}\text{C}$ NMR Spectra

The  $^{13}\text{C}$  NMR spectral splitting pattern was similar to that of free ligand[16] (Table 4). The methyl carbon ( $-\text{CH}_3$ ) attached to the tolyl ring resonates in the region 16.5-21.1 ppm in these complexes. The carbon nucleus of the tolyl group resonates in the region 111.2-155.5 ppm. The chemical shifts for C–O carbon were found in the region 153.1-155.5 ppm indicated inductive effect in the C–O bond. The chemical shift for C–( $\text{CH}_3$ ) carbon nucleus was observed in the region 121.1-128.4 ppm.

### Mass Spectra

The mass spectra of few representative cerium(III) complexes have been carried out and these have shown

the molecular ion peak  $[\text{M}^+]$  at 1068.2 (m/z) (**1**) and 1274.4 (m/z) (**4**). The fragmented species produced after the consecutive removal of different groups also indicate their formation in the mass spectra. The occurrence of molecular ion peak in the complexes is supporting the monomeric nature of the complexes while the rest of the diagnostic peaks were found to be consistent with the possible fragmentation pattern. Moreover, the complex **4** contains chlorine atom that results in appearance of isotopic peaks in the mass spectrum. The masses of the fragmented ions, listed in the table, are calculated using one chlorine atom mass equal to 35 amu, as it is the most abundant isotope of chlorine atom. The possible fragments formed on the basis of mass spectrum of these cerium(III) dithiophosphates is given in Table 5.

**Table 4**  $^{13}\text{C}$  NMR spectral data of the ditolyldithiophosphates of cerium(III) (in ppm).

S. No.	$\text{CH}_3$	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
1.	18.1	153.1	123.4*	129.0	127.5	130.5	126.3
2.	19.7	155.2	119.0	121.1*	126.4	128.7	129.3
3.	21.1	154.6	115.8	129.3	128.4*	129.3	114.8
4.	19.2	155.0	111.2	123.3*	135.7'	128.5	116.8
5.	16.5	155.5	115.0*	127.6	126.8	130.7	119.6

\* = C– $\text{CH}_3$ , ' = C–Cl

**Table 5** Mass spectral data of the ditolyldithiophosphates of cerium(III).

S. No.	M. W.	m/z, relative intensities of the ions and assignment
1.	1068.2	[M <sup>+</sup> ] 1068.2 (10) [ {(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> } <sub>3</sub> Ce], [M <sup>+</sup> ] 758.8 (21) [ {(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> } <sub>2</sub> Ce] <sup>+</sup> , [M <sup>+</sup> ] 698.7 (28) [ {(C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> } <sub>2</sub> Ce] <sup>+</sup> , [M <sup>+</sup> ] 279.3 (48) [(C <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PS <sub>2</sub> ] <sup>-</sup> , [M <sup>+</sup> ] 358.4 (31) [ {(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O)P(O)S <sub>2</sub> }Ce] <sup>+</sup> , [M <sup>+</sup> ] 202.3 (56) [(o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O)PS <sub>2</sub> ] <sup>-</sup> , [M <sup>+</sup> ] 107.1 (91) [CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O] <sup>-</sup>
4.	1274.9	[M <sup>+</sup> ] 1274.9 (6), 1187.5 (2) [ {(p-Cl-m-CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub> O) <sub>2</sub> PS <sub>2</sub> } <sub>3</sub> Ce], [M <sup>+</sup> ] 896.6 (15), 809.5 (5) [ {(p-Cl-m-CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub> O) <sub>2</sub> PS <sub>2</sub> } <sub>2</sub> Ce] <sup>+</sup> , [M <sup>+</sup> ] 836.5 (21), 749.5 (7) [ {p-Cl-C <sub>6</sub> H <sub>3</sub> O) <sub>2</sub> PS <sub>2</sub> } <sub>2</sub> Ce] <sup>+</sup> , [M <sup>+</sup> ] 694.7 (48) [ {(C <sub>6</sub> H <sub>3</sub> O) <sub>2</sub> PS <sub>2</sub> } <sub>2</sub> Ce] <sup>+</sup> , [M <sup>+</sup> ] 277.3 (48) [(C <sub>6</sub> H <sub>3</sub> O) <sub>2</sub> PS <sub>2</sub> ] <sup>-</sup> , [M <sup>+</sup> ] 202.3 (56) [(m-CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub> O)PS <sub>2</sub> ] <sup>-</sup> , [M <sup>+</sup> ] 141.5 (91), 143.5 (30) [p-Cl-m-CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub> O] <sup>-</sup> [M <sup>+</sup> ] 106.1 (91) [m-CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub> O] <sup>-</sup>

Where, bracket = m/z; parentheses = intensities in %

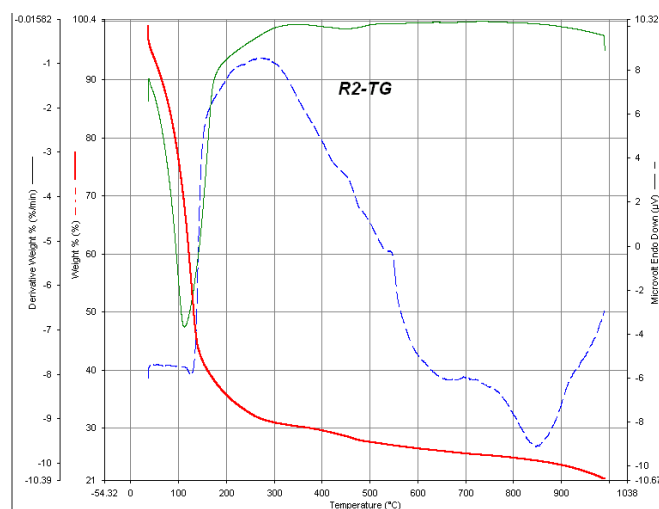
### Thermogravimetric Analysis

Thermal behavior of [ {(p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>PS<sub>2</sub> }<sub>3</sub>Ce] has been studied by using various thermoanalytical techniques which include Differential thermogravimetry (DTG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) under nitrogen flow at a uniform rate of 10°C min<sup>-1</sup> from room temperature to 1000°C. The recorded thermograph (Figure 1) was first analyzed to obtain information about the percentage of weight loss at different temperatures. From the curve, it is clear that the complex is thermally unstable and its mass is found to be lost continuously as a function of temperature. The thermal decomposition takes place in three different steps starting from 35°C to 1000°C with the total observed mass loss in the entire three cases are compiled in Table 6. The first stage of decomposition start from 35°C and goes up to 141°C with the observed weight loss is 56.15%. During this decomposition stage a broad and sharp endothermic peak is observed at

110°C which might be due to the conversion of dithiophosphate complexes to dithiometaphosphate fragment corresponding to [Ce(S<sub>2</sub>PO)<sub>3</sub>] (the calculated weight loss is 55.68%) as an intermediate product, which agrees with thermogravimetric data for dithiophosphates [20]. The second stage of decomposition starts at around 141°C and is completed at around 206°C. This stage of decomposition corresponds to weight loss of 64.76% and this mass loss is due to the transformation of Cerium (III) trisulfide in the forms as α-Ce<sub>2</sub>S<sub>3</sub>, β-Ce<sub>2</sub>S<sub>3</sub> and γ-Ce<sub>2</sub>S<sub>3</sub> with different structures [21, 22] observed at very high temperature. The third stage decomposition stage leading to the formation of the final residue at 986.7°C corresponds to CeS<sub>2</sub> (the calculated weight loss is 80.88%) is 78.62% of the initial weight of the sample with the oxidation of Ce(III) to Ce(IV). The DSC thermograph shows the wide and broad endothermic at above 800 °C may be attributed to the transition of structure from Ce<sub>2</sub>S<sub>3</sub> to the final product CeS<sub>2</sub>.

**Table 6.** Results of thermal decomposition for different temperature ranges with observed and calculated weight loss of [ {(p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>PS<sub>2</sub> }<sub>3</sub>Ce].

Fragment (weight)	Temperature	Calculated		Observed	
		Wt. loss (%)	Wt left (%)	Wt. loss (%)	Wt left (%)
[Ce(S <sub>2</sub> PO) <sub>3</sub> ]	141°C	55.68	44.32	56.15	43.85
Ce <sub>2</sub> S <sub>3</sub>	206°C	64.76	35.24	64.80	35.20
CeS <sub>2</sub>	986°C	80.88	19.12	78.62	21.38



**Figure 1:** Thermogravimetric curve for complex  $[\{(p\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_3\text{Ce}]$ .

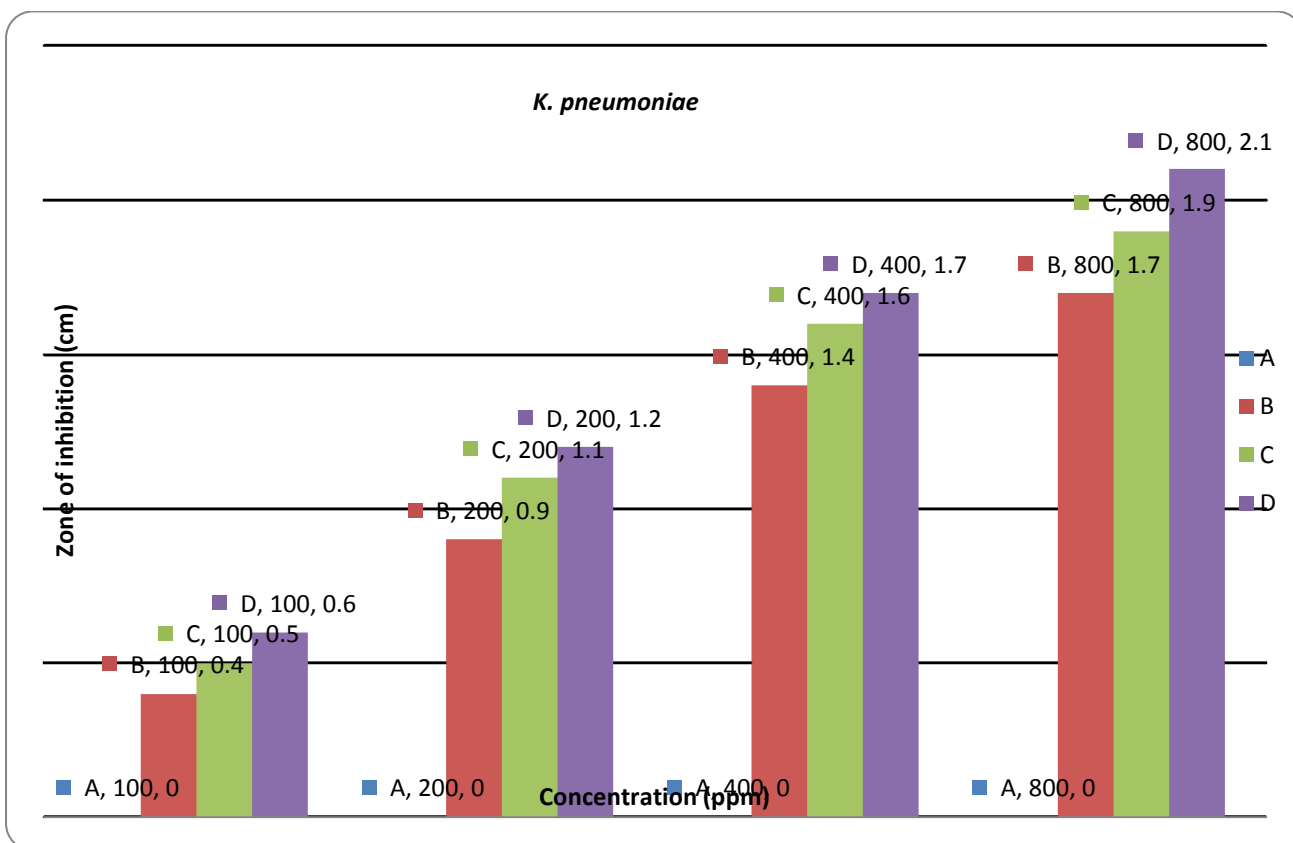
### Antimicrobial Activity

The antibacterial screening of these complexes also exhibited significant inhibition of bacterial strains gram-negative, *Klebsiellapneumoniae* and gram-positive, *Bacillus cereus* and fungus *Penicilliumchrysogenum* with increasing concentration of the complexes. The observed zone of inhibition for each concentration of the complexes has been given in the Table 7 and graphical comparison in Figure 2 (a-c) which also shows high antimicrobial activity of these complexes. This study shows that these novel cerium complexes can be of valuable therapeutic index and can be used to treat various infectious disease caused by the microbes. However, further studies are needed to better evaluate the potential effectiveness of these complexes

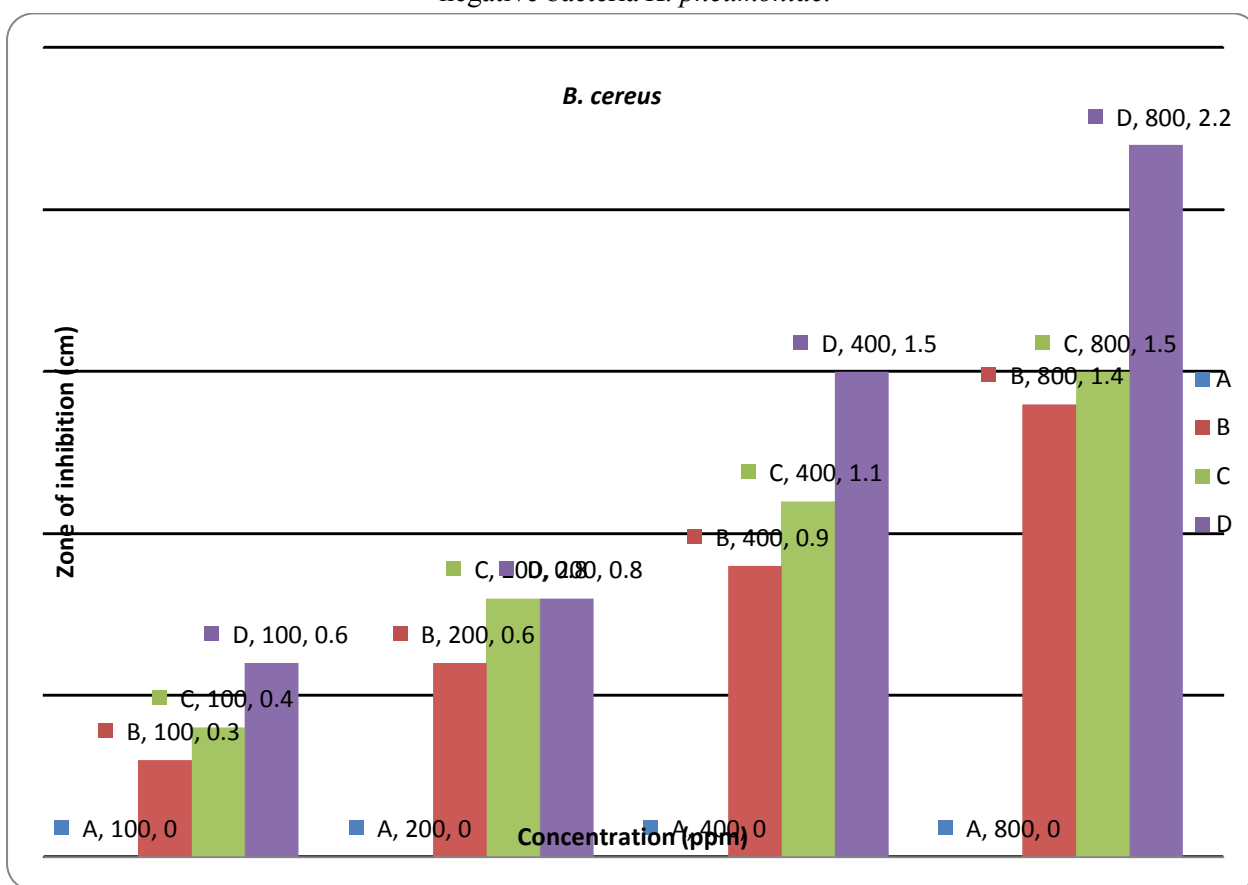
as the antimicrobial agents. The present results will form the basis for selection of bacterial species for further investigation in the potential discovery of new bioactive cerium compounds. The increased activity of the metal complexes in comparison to free ligands is explained on the basis of Overtone's concept and Tweedy's chelation theory[23]. The complex  $[\{(p\text{-Cl-}m\text{-CH}_3\text{C}_6\text{H}_3\text{O})_2\text{PS}_2\}_3\text{Ce}]$  showed maximum bioactive potential against both bacterial species as well as the fungal species under study which can be attributed to the formation of chloride bridges between biomolecules of the organism and the complex leading to inactivation of their biological processes.

**Table 7.** Antibacterial screening results of the ligands and ditolyldithiophosphates of cerium(III).

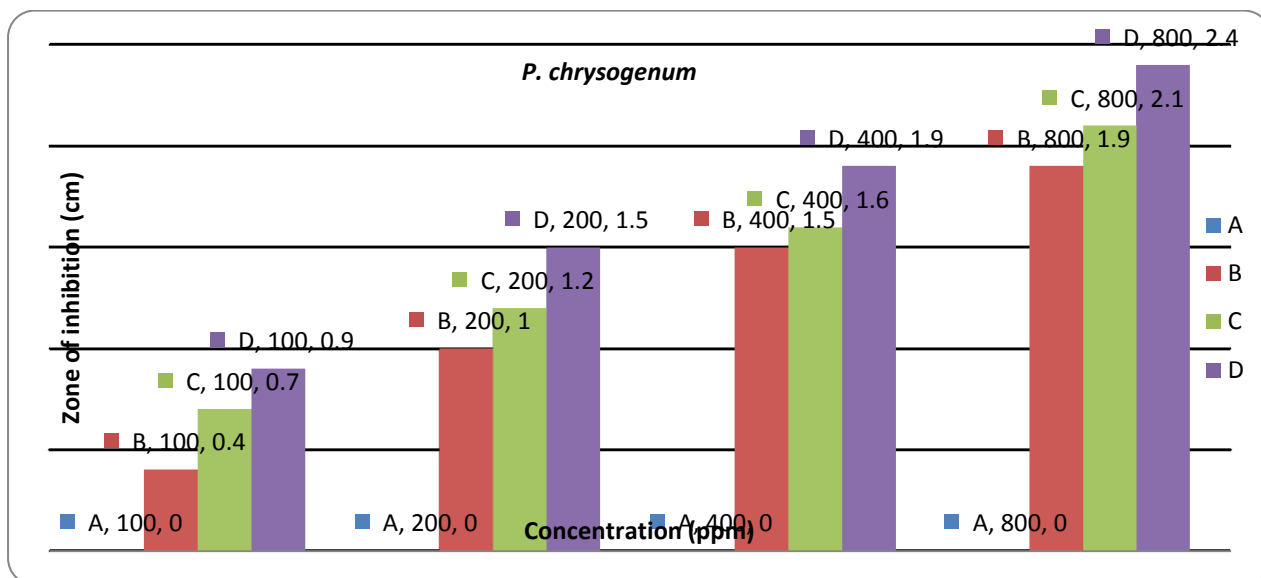
Ligand/Complex	Zone of inhibition (in cm)											
	<i>Klebsiellapneumoniae</i> (-)				<i>Bacillus cereus</i> (+)				<i>Penicillium chrysogenum</i>			
	100	200	400	800	100	200	400	800	100	200	400	800
$[\{o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}\text{Na}]$ (A)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$[\{p\text{-Cl-}m\text{-CH}_3\text{C}_6\text{H}_3\text{O})_2\text{PS}_2\}\text{Na}]$ (B)	0.4	0.9	1.4	1.7	0.3	0.6	0.9	1.4	0.4	1.0	1.5	1.9
$[\{o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}_3\text{Ce}]$ (C)	0.5	1.1	1.6	1.9	0.4	0.8	1.1	1.5	0.7	1.2	1.6	2.1
$[\{p\text{-Cl-}m\text{-CH}_3\text{C}_6\text{H}_3\text{O})_2\text{PS}_2\}_3\text{Ce}]$ (D)	0.6	1.2	1.7	2.1	0.6	0.8	1.5	2.2	0.9	1.5	1.9	2.4



**Figure 2(a) :** Graphical comparison of antibacterial screening results of all ligands and complexes against gram negative bacteria *K. pneumoniae*.



**Figure 2(b):** Graphical comparison of antibacterial screening results of all ligands and complexes against gram negative bacteria *B. cereus*.

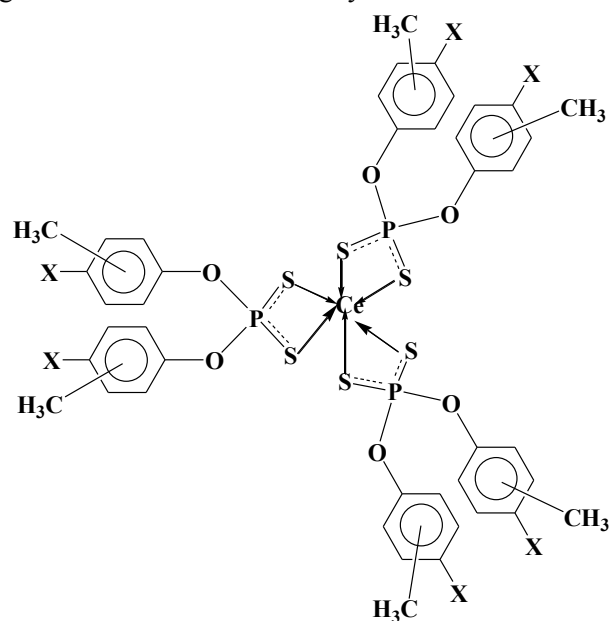


**Figure 2(c):** Graphical comparison of antifungal screening results of all ligands and complexes against gram negative fungus *P. chrysogenum*.

#### IV. CONCLUSION

The the current spectroscopic and thermal analysis elemental analysis, mass, IR, NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ) of the new synthesized complexes of ditolyldithiophosphates of cerium(III) in conjunction with the literature reports[12-16] put forth a probable structure for these complexes. It is interesting to note that appearance of new bands was observed in the IR spectra of these complexes in comparison to the parent dithiophosphate ligands. A singlet with shifting compared to parent ligand for the phosphorus atom of the dithiophosphatomoiety indicates the bidentate mode of chelation by dithiophosphate ligand as well as equivalent nature of the phosphorus atom in these complexes. Therefore, six folded coordination may tentatively be proposed for the cerium(III) *tris-O,O'*-di(*o*-, *m*-, *p*- and *p*-Cl-*m*-)tolylidithiophosphate. The  $\Delta\nu$  value for the  $\nu\text{P-S}_{(\text{asym})}$  and  $\nu\text{P-S}_{(\text{sym})}$  bands for both the moieties in comparison to the parent dithiophosphate ligands also indicate the formation of these complexes. Hexacoordinate geometry may be proposed around the cerium(III) atom (Figure 3). The thermal study reveals a three step decomposition process involving the formation of the dithiometaphosphate as the characteristic intermediate and finally completely decomposes above  $800^\circ\text{C}$  as  $\text{CeS}_2$  as the final residue. The complexes are found to have higher biological activities as compared to the respective ligand. The biological activity of these complexes against bacteria-*Klebsiellapneumoniae* and *Bacillus*

*cerus* and fungus-*Penicilliumchrysogenum* indicated significant antimicrobial activity.



**Figure 3:** Proposed octahedral structure of *tris-O,O'*-di(*o*-, *m*-, *p*- and *p*-Cl-*m*-tolylidithiophosphates) of cerium(III) (1-4); X = H (1,2),  $\text{CH}_3$  (3) or Cl (4).

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