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# Syntheses and Characterization of Mixed Ligand Dithiophosphates of Cerium(III) and their Adducts with Phosphorus Donor Bases

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## Abstract

The mixed ligand dithiophosphato complexes of the composition  $[(o-, m-, p-CH_3C_6H_4O)_2PS_2]_2\{(OCH_2)C(CH_3)_2(CH_2O)PS_2\}Ce$  have also been isolated by the reaction of cerium chloride,  $CeCl_3$ , sodium ditolylphosphorodithioates, (*o*-, *m*-, *p*- $CH_3C_6H_4O$ ) $_2PS_2Na$ , and sodium neopentylphosphorodithioate,  $OCH_2C(CH_3)_2CH_2OPS_2Na$ , in 1:2:1 molar ratio under anhydrous conditions. These complexes formed adducts with the nitrogen and phosphorus donor molecules by straight forward reaction of these complexes with donor ligands. These adducts have the composition of the type  $[(o-, m-, p-CH_3C_6H_4O)_2PS_2]_2\{(OCH_2)C(CH_3)_2(CH_2O)PS_2\}Ce.2P(C_6H_5)_3$ . These complexes have been characterized by elemental analysis, mass, IR and heteronuclear NMR ( $^1H$ ,  $^{13}C$  and  $^{31}P$ ) spectroscopic studies. Coordination numbers of six and eight are suggested around the cerium atom in these complexes, leading to octahedral and dodecahedral geometries.

**Keywords** Cerium, Phosphorus compounds, Total synthesis, Spectroscopy

## Introduction

Versatile coordination chemistry exhibited by the rare earth elements has been of interest since decades as their complexes have found significant role in chemical[1], medical,[2] and industrial[3] processes. Cerium is the most abundant lanthanide and finds extensive applicability due to its catalytic behavior[4], in catalytic converters[5], in flat-screen TVs, low-energy light bulbs and floodlights[6]. The dithiophosphate chemistry of transition metals is vast, due to their fascinating modes of bonding[7-9] as well as the increasing applications in industry[10] and agriculture[11]. There is scarce of reports on lanthanides with such ligands and ditolyl dithiophosphates 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 novel mixed ligand dithiophosphates of cerium(III).

## Experimental

Exclusion of moisture was carefully done throughout the experimental manipulations by using standard Schlenk techniques. Methanol and chloroform were dried over  $CaCO_3$  and  $P_2O_5$ , respectively. Ligands were prepared by reported procedure[16]. Cerium was estimated gravimetrically as  $Ce_2O_3$ [17]. Elemental analyses (C, H, N, S) were conducted using the Elemental Analyser Vario EL-III, their results were found to be in good agreement ( $\pm 0.3\%$ ) with the calculated values. Infrared spectra were recorded in the range of  $4000-400\text{ cm}^{-1}$  on a Shimadzu 8201 PC spectrophotometer. The  $^1H$  and  $^{13}C$  NMR spectra were recorded in  $CDCl_3$  on a Bruker Avance II 400 (300 MHz) using TMS as internal reference. The  $^{31}P$  NMR spectra were recorded in  $CDCl_3$  using  $H_3PO_4$  (85%) as external reference on a Bruker Avance II 400 (300 MHz). The ESI mass spectra were recorded on ESI-esquires 3000 Bruker Daltonics spectrophotometer.

### Synthesis of $[\{(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})\text{PS}_2\}]_2\{(\text{OCH}_2)\text{C}(\text{CH}_3)_2(\text{CH}_2\text{O})\text{PS}_2\}\text{Ce}]$ (1)

To a methanolic solution ( $\sim 15\text{ cm}^3$ ) of 0.56 g of cerium chloride (heptahydrated) (1.50 mmol), a methanolic solution ( $\sim 30\text{ cm}^3$ ) of 1.00 g of sodium *O,O*-*o*-ditolyldithiophosphate (3.01 mmol) was added dropwise with constant stirring at room temperature. After five hours of stirring, a methanolic solution ( $\sim 10\text{ cm}^3$ ) of 0.33 g of sodium salt of neopentylene dithiophosphoric acid (1.50 mmol) was added dropwise with constant stirring. The contents were stirred for three hours followed by refluxing for five hours. Turbidity appeared due to formation of sodium chloride. Now, methanol was removed under reduced pressure, which left a solid residue. Subsequently, the desired product was extracted from chloroform after stirring for overnight. The precipitated sodium chloride was separated by filtration using alkoxy funnel fitted with G-4 disc. Evaporation of chloroform in *vacuo* resulted in the formation of the desired complex,  $[\{(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}]_2\{(\text{OCH}_2)\text{C}(\text{CH}_3)_2(\text{CH}_2\text{O})\text{PS}_2\}\text{Ce}]$ , (**1**) as white solid. Yield: 89 %; *Anal. Calc.* for  $\text{C}_{33}\text{H}_{38}\text{O}_6\text{P}_3\text{S}_6\text{Ce}$ : C, 41.46; H, 4.01; S, 20.12; Ce, 14.66, Found: C, 41.14; H, 3.85; S, 20.01; Ce, 14.54; IR ( $\text{cm}^{-1}$ ) = tolyl dithiophosphate moiety: 1109.1, s [ $\nu(\text{P})\text{-O-C}$ ], 937.8, s [ $\nu(\text{P})\text{-O-(C)}$ ], 683.1, s [ $\nu\text{P S}$ ], 559.5, m [ $\nu\text{P-S}$ ], neopentylene dithiophosphate moiety: 999.8, s [ $\nu(\text{P})\text{-O-C}$ ], 792.4, s [ $\nu(\text{P})\text{-O-(C)}$ ], 598.7, s [ $\nu\text{P S}$ ], 552.0, m [ $\nu\text{P-S}$ ], 339.7, w [ $\nu\text{Ce-S}$ ]  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) = 2.2 (s, 12 H,  $\text{CH}_3$ , tolyl), 0.9 (s, 6 H,  $\text{CH}_3$ , neopentyl), 3.9 (s, 4 H,  $\text{CH}_2$ , neopentyl), 6.6 (d, 8 H, *ortho*,  $J = 8.1$ ), 6.9 (d, 8 H, *meta*,  $J = 8.1$ ) ppm;  $^{31}\text{P NMR}$  ( $\text{CDCl}_3$ ) = 91.2 (tolyl moiety), 82.3 (neopentylene moiety) ppm;  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ) = 16.4 ( $\text{CH}_3$ , tolyl), 21.8 ( $\text{CH}_3$ , neopentyl), 32.8 ( $>\text{C}<$ , neopentyl), 75.3 ( $\text{CH}_2$ , neopentyl), 119.2 (*C-ortho*), 128.1 (*C-CH}\_3*), 129.1 (*C-para*), 129.7-133.2 (*C-meta*), 148.3 (*C-O*) ppm.

### Synthesis of $[\{(m\text{-CH}_3\text{C}_6\text{H}_4\text{O})\text{PS}_2\}]_2\{(\text{OCH}_2)\text{C}(\text{CH}_3)_2(\text{CH}_2\text{O})\text{PS}_2\}\text{Ce}]$ (2)

The synthesis of complex **2** was carried out as described for complex **1**; 1.00 g of sodium *O,O*-*m*-ditolyldithiophosphate (3.01 mmol), 0.56 g of cerium chloride (heptahydrated) (1.51 mmol) and 0.33 g of sodium salt of neopentylene dithiophosphoric acid (1.50 mmol) were used to give **2** as white solid. Yield: 87 %; *Anal. Calc.* for  $\text{C}_{33}\text{H}_{38}\text{O}_6\text{P}_3\text{S}_6\text{Ce}$ : C, 41.46; H, 4.01; S, 20.12; Ce, 14.66, Found: C, 41.13; H, 3.87; S, 20.03; Ce, 14.54; IR ( $\text{cm}^{-1}$ ) = tolyl dithiophosphate moiety: 1050.6, s [ $\nu(\text{P})\text{-O-C}$ ], 941.4, s [ $\nu(\text{P})\text{-O-(C)}$ ], 685.5, s [ $\nu\text{P S}$ ], 563.8, m [ $\nu\text{P-S}$ ], neopentylene dithiophosphate moiety: 995.4, s [ $\nu(\text{P})\text{-O-C}$ ], 780.2, s [ $\nu(\text{P})\text{-O-(C)}$ ], 608.9, s [ $\nu\text{P S}$ ], 547.2, m [ $\nu\text{P-S}$ ], 337.8, w [ $\nu\text{Ce-S}$ ]  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) = 2.3 (s, 12 H,  $\text{CH}_3$ , tolyl), 1.0 (s, 6 H,  $\text{CH}_3$ , neopentyl), 4.3 (s, 4 H,  $\text{CH}_2$ , neopentyl), 6.6-6.7 (m, 8 H, *ortho*,  $J = 8.2$ ), 6.9 (d, 4 H, *para*,  $J = 8.2$ ), 7.1 (t, 4 H, *meta*,  $J = 8.2$ ) ppm;  $^{31}\text{P NMR}$  ( $\text{CDCl}_3$ ) = 93.8 (tolyl moiety), 81.4 (neopentylene moiety) ppm;  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ) = 20.2 ( $\text{CH}_3$ , tolyl), 21.9 ( $\text{CH}_3$ , neopentyl), 32.7 ( $>\text{C}<$ , neopentyl), 75.0 ( $\text{CH}_2$ , neopentyl), 111.4-130.8 (*C-ortho*), 119.8 (*C-para*), 121.8 (*C-meta*), 123.6 (*C-CH}\_3*), 153.8 (*C-O*), 131.4-132.7 ( $\text{P}(\text{C}_6\text{H}_5)_3$ ) ppm; ESI-MS:  $m/z$  (%) = 956.1 (6)  $[\{(m\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}]_2\{(\text{OCH}_2)\text{C}(\text{CH}_3)_2(\text{CH}_2\text{O})\text{PS}_2\}\text{Ce}]$ , 524.6 (15)  $[(\text{OCH}_2)\text{C}(\text{CH}_3)_2(\text{CH}_2\text{O})\text{PS}_2]\text{Ce}\{\text{S}_2\text{P}(\text{OC}_6\text{H}_4)\}^+$ , 358.4 (42)  $[\{(m\text{-CH}_3\text{C}_6\text{H}_4\text{O})\text{P}(\text{O})\text{S}_2\}\text{Ce}]^+$ , 337.4 (32)  $[(\text{OCH}_2)\text{C}(\text{CH}_3)_2(\text{CH}_2\text{O})\text{PS}_2]\text{Ce}^+$ , 309.3 (86)  $[(m\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2]^+$ , 107.2 (98)  $[m\text{-CH}_3\text{C}_6\text{H}_4\text{O}]^+$ , 102.5 (67)  $[(\text{OCH}_2)_2\text{C}(\text{CH}_3)_2]^+$ .

### Synthesis of $[\{(p\text{-CH}_3\text{C}_6\text{H}_4\text{O})\text{PS}_2\}]_2\{(\text{OCH}_2)\text{C}(\text{CH}_3)_2(\text{CH}_2\text{O})\text{PS}_2\}\text{Ce}]$ (3)

The synthesis of complex **3** was carried out as described for complex **1**; 1.00 g of sodium *O,O*-*p*-ditolyldithiophosphate (3.01 mmol), 0.56 g of cerium chloride (heptahydrated) (1.51 mmol) and 0.33 g of sodium salt of neopentylene dithiophosphoric acid (1.50 mmol) were used to give **3** as white solid. Yield: 91 %; *Anal. Calc.* for  $\text{C}_{33}\text{H}_{38}\text{O}_6\text{P}_3\text{S}_6\text{Ce}$ : C, 41.46; H, 4.01; S, 20.12; Ce, 14.66, Found: C, 41.24; H, 3.86; S, 20.05; Ce, 14.58; IR ( $\text{cm}^{-1}$ ) = tolyl dithiophosphate moiety: 1211.1, s [ $\nu(\text{P})\text{-O-C}$ ], 945.9, s [ $\nu(\text{P})\text{-O-(C)}$ ], 691.1, s [ $\nu\text{P S}$ ], 552.7, m [ $\nu\text{P-S}$ ], neopentylene dithiophosphate moiety: 998.2, s [ $\nu(\text{P})\text{-O-C}$ ], 775.7, s [ $\nu(\text{P})\text{-O-(C)}$ ], 608.0, s [ $\nu\text{P S}$ ], 463.4, m [ $\nu\text{P-S}$ ], 335.3, w [ $\nu\text{Ce-S}$ ]  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) = 2.2 (s, 12 H,  $\text{CH}_3$ , tolyl), 0.9 (s, 6 H,  $\text{CH}_3$ , neopentyl), 3.9 (s, 4 H,  $\text{CH}_2$ , neopentyl), 6.6 (d, 8 H, *ortho*,  $J = 8.2$ ), 6.9 (d, 8 H, *meta*,  $J = 8.1$ ) ppm;  $^{31}\text{P NMR}$  ( $\text{CDCl}_3$ ) = 94.8 (tolyl moiety), 80.8 (neopentylene moiety) ppm;  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ) =

19.1 (CH<sub>3</sub>, tolyl), 28.7 (CH<sub>3</sub>, neopentyl), 32.1 (>C<, neopentyl), 73.4 (CH<sub>2</sub>, neopentyl), 114.8.2 (C-*ortho*), 127.3 (C-CH<sub>3</sub>), 129.3 (C-*meta*), 154.6 (C-O) ppm.

**Synthesis of  $[\{(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})\text{PS}_2\}]_2\{(\text{OCH}_2)\text{C}(\text{CH}_3)_2(\text{CH}_2\text{O})\text{PS}_2\}\text{Ce}\cdot 2\text{P}(\text{C}_6\text{H}_5)_3\]$  (4)**

To a methanolic solution (~15 cm<sup>3</sup>) of 0.56 g of cerium chloride (heptahydrated) (1.51 mmol), a methanolic solution (~30 cm<sup>3</sup>) of 1.00 g of sodium *O,O*-*o*-ditolyldithiophosphate (3.01 mmol) was added dropwise with constant stirring at room temperature. After five hours of stirring, a methanolic solution (~10 cm<sup>3</sup>) of 0.33 g of sodium salt of neopentylene dithiophosphoric acid (1.50 mmol) was added dropwise with constant stirring. The contents were stirred for three hours followed by refluxing for five hours. Turbidity appeared due to formation of sodium chloride. Now, a methanol solution (~10 cm<sup>3</sup>) of 0.79 g of triphenylphosphine, P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> (3.01 mmol) was added with constant stirring at room temperature. The contents were stirred for three hours followed by refluxing for five hours. Evaporation of methanol in *vacuo* resulted in the formation of the desired complex,  $[\{(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2\text{PS}_2\}]_2\{(\text{OCH}_2)\text{C}(\text{CH}_3)_2(\text{CH}_2\text{O})\text{PS}_2\}\text{Ce}\cdot 2\text{P}(\text{C}_6\text{H}_5)_3\]$ , (**4**) as white solid. Yield: 83 %; *Anal. Calc.* for C<sub>69</sub>H<sub>68</sub>O<sub>6</sub>P<sub>5</sub>S<sub>6</sub>Ce: C, 55.97; H, 4.63; S, 12.99; Ce, 9.46, Found: C, 55.87; H, 4.58; S, 12.71; Ce, 9.34; IR (cm<sup>-1</sup>) = tolyl dithiophosphate moiety: 1106.2, s [ν(P)-O-C], 937.8, s [νP-O-(C)], 683.2, s [νP S], 565.9, m [νP-S], neopentylene dithiophosphate moiety: 999.1, s [ν(P)-O-C], 794.3, s [νP-O-(C)], 600.0, s [νP S], 542.9, m [νP-S], 334.5, w [νCe-S], 331.7, w [νCe-P] cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) = 2.4 (s, 12 H, CH<sub>3</sub>, tolyl), 1.1 (s, 6 H, CH<sub>3</sub>, neopentyl), 4.4 (s, 4 H, CH<sub>2</sub>, neopentyl), 6.7 (d, 4 H, *ortho*, *J* = 8.2), 6.9-7.1 (m, 8 H, *meta*, *J* = 8.2), 7.3 (t, 4 H, *para*, *J* = 8.2), 7.5-7.7 (m, 30 H, C<sub>6</sub>H<sub>5</sub>, *J* = 8.2) ppm; <sup>31</sup>P NMR (CDCl<sub>3</sub>) = 94.5 (tolyl moiety), 84.1 (neopentylene moiety), -4.8 (P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) = 16.4 (CH<sub>3</sub>, tolyl), 21.8 (CH<sub>3</sub>, neopentyl), 32.8 (>C<, neopentyl), 75.3 (CH<sub>2</sub>, neopentyl), 119.2 (C-*ortho*), 128.1 (C-CH<sub>3</sub>), 129.1 (C-*para*), 129.7-133.2 (C-*meta*), 148.3 (C-O) ppm.

**Synthesis of  $[\{(m\text{-CH}_3\text{C}_6\text{H}_4\text{O})\text{PS}_2\}]_2\{(\text{OCH}_2)\text{C}(\text{CH}_3)_2(\text{CH}_2\text{O})\text{PS}_2\}\text{Ce}\cdot 2\text{P}(\text{C}_6\text{H}_5)_3\]$  (5)**

Complex **5** was prepared by the same procedure as described for complex **3**; 1.00 g of sodium *O,O*-*p*-ditolyldithiophosphate (3.01 mmol), 0.56 g of cerium chloride (heptahydrated) (1.51 mmol), 0.33 g of sodium salt of neopentylene dithiophosphoric acid (1.50 mmol) and 0.79 g of triphenylphosphine, P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> (3.01 mmol) were used to give **5** as white solid. Yield: 90 %; *Anal. Calc.* for C<sub>69</sub>H<sub>68</sub>O<sub>6</sub>P<sub>5</sub>S<sub>6</sub>Ce: C, 55.97; H, 4.63; S, 12.99; Ce, 9.46, Found: C, 55.89; H, 4.54; S, 12.85; Ce, 9.31; IR (cm<sup>-1</sup>) = tolyl dithiophosphate moiety: 1087.7, s [ν(P)-O-C], 940.7, s [νP-O-(C)], 695.9, s [νP S], 563.8, m [νP-S], neopentylene dithiophosphate moiety: 996.8, s [ν(P)-O-C], 805.1, s [νP-O-(C)], 609.0, s [νP S], 546.5, m [νP-S], 339.6, w [νCe-S], 332.1, w [νCe-P] cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) = 2.3 (s, 12 H, CH<sub>3</sub>, tolyl), 1.0 (s, 6 H, CH<sub>3</sub>, neopentyl); 4.2 (s, 4 H, CH<sub>2</sub>, neopentyl), 6.7-7.1 (m, 8 H, *ortho*, *J* = 8.1), 6.8 (d, 4 H, *para*, *J* = 8.1), 6.9 (m, 4 H, *meta*, *J* = 8.2), 7.5-7.8 (m, 30 H, C<sub>6</sub>H<sub>5</sub>, *J* = 8.2) ppm; <sup>31</sup>P NMR (CDCl<sub>3</sub>) = 91.5 (tolyl moiety), 81.4 (neopentylene moiety), -4.9 (P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>) = 20.2 (CH<sub>3</sub>, tolyl), 21.9 (CH<sub>3</sub>, neopentyl), 32.7 (>C<, neopentyl), 75.0 (CH<sub>2</sub>, neopentyl), 111.4-130.8 (C-*ortho*), 119.8 (C-*para*), 121.8 (C-*meta*), 123.6 (C-CH<sub>3</sub>), 153.8 (C-O), 131.4-132.7 (P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>) ppm.

**Synthesis of  $[\{(p\text{-CH}_3\text{C}_6\text{H}_4\text{O})\text{PS}_2\}]_2\{(\text{OCH}_2)\text{C}(\text{CH}_3)_2(\text{CH}_2\text{O})\text{PS}_2\}\text{Ce}\cdot 2\text{P}(\text{C}_6\text{H}_5)_3\]$  (6)**

Complex **6** was prepared by the same procedure as described for complex **4**; 1.00 g of sodium *O,O*-*p*-ditolyldithiophosphate (3.01 mmol), 0.56 g of cerium chloride (heptahydrated) (1.51 mmol), 0.33 g of sodium salt of neopentylene dithiophosphoric acid (1.50 mmol) 0.79 g of triphenylphosphine, P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> (3.01 mmol) were used to give **6** as white solid. Yield: 89 %; *Anal. Calc.* for C<sub>69</sub>H<sub>68</sub>O<sub>6</sub>P<sub>5</sub>S<sub>6</sub>Ce: C, 55.97; H, 4.63; S, 12.99; Ce, 9.46, Found: C, 55.77; H, 4.52; S, 12.79; Ce, 9.39; IR (cm<sup>-1</sup>) = tolyl dithiophosphate moiety: 1087.1, s [ν(P)-O-C], 930.1, s [νP-O-(C)], 699.2, s [νP S], 560.2, m [νP-S], neopentylene dithiophosphate moiety: 994.4, s [ν(P)-O-C], 794.0, s [νP-O-(C)], 604.2, s [νP S], 541.6, m [νP-S], 339.4, w [νCe-S], 331.6, w [νCe-P] cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) = 2.2 (s, 12 H, CH<sub>3</sub>, tolyl), 0.9 (s, 6 H, CH<sub>3</sub>, neopentyl), 3.9 (s, 4 H, CH<sub>2</sub>, neopentyl), 6.6 (d, 8 H, *ortho*, *J* = 8.2), 6.9 (d, 8 H, *meta*, *J* = 8.1) ppm; <sup>31</sup>P NMR (CDCl<sub>3</sub>) = 92.5 (tolyl



These complexes and adducts are soluble in common organic solvents (benzene, toluene, acetonitrile, methanol, chloroform), however, insoluble in solvents like *n*-hexane and carbon tetrachloride. These complexes appear to be bit moisture sensitive but can be stored under anhydrous conditions for longer periods of time. These complexes are non-volatile even under the reduced pressure. The elemental analyses (C, H, N, S and Ce) were found consistent with the molecular formula of these complexes.

### ***Infrared spectra***

IR spectra of these complexes (**1-6**) were recorded in the range of 4000-200  $\text{cm}^{-1}$  as KBr pellets and the tentative assignments were made on the basis of relevant literature reports [12-16]. The comparison of IR spectra of these complexes with starting materials has also shown significant and characteristic changes and shifting of bands. Two strong intensity bands were observed in the region 1211.1-1050.6  $\text{cm}^{-1}$  and 945.9-930.1  $\text{cm}^{-1}$ , which may be ascribed to the (P)–O–C and P–O–(C) vibrations of the ditolyldithiophosphate moiety, respectively. Furthermore, two strong intensity bands were observed in the region 999.8-994.4  $\text{cm}^{-1}$  and 805.1-775.7  $\text{cm}^{-1}$  in the spectra of the mixed ligand complexes, which may be ascribed to the (P)–O–C and P–O–(C) vibrations of the neopentylenedithiophosphate moiety, respectively. This is indicative of the presence of two types of dithiophosphate moieties. The bands for P=S and P–S of the ditolyldithiophosphate moiety were observed in the region 699.2-683.1  $\text{cm}^{-1}$  and 565.9-552.7  $\text{cm}^{-1}$ . The bands observed in the region 609.0-598.7  $\text{cm}^{-1}$  and 552.0-463.4  $\text{cm}^{-1}$  in the spectra of the mixed ligand complexes have been assigned to P=S and P–S vibrations, respectively, for the neopentylenedithiophosphate moiety. The bands due to P=S and P–S vibrations have depicted a shift of 10-30  $\text{cm}^{-1}$  toward the lower frequency region in comparison to the parent dithiophosphate ligands. This shift of P–S vibration is perhaps due to bidentate mode of bonding by dithiophosphate ligands. The presence of a band for Ce–S in the region 339.7-334.5  $\text{cm}^{-1}$  in the spectra of these complexes is indicative of the formation of cerium-sulfur bond. IR spectra have revealed the presence of bands for Ce–P in the complexes **4-6** in the region 332.1-331.6  $\text{cm}^{-1}$ .

### ***<sup>1</sup>H NMR spectra***

The <sup>1</sup>H NMR spectra of these complexes recorded in CDCl<sub>3</sub> show the characteristic proton resonance of the corresponding tolyl, benzyl and neopentylene protons. In the <sup>1</sup>H NMR spectra, the chemical shift for the methyl (–CH<sub>3</sub>) protons of the tolyl ring and were observed in the regions 2.0-2.4 ppm as singlet. The chemical shifts for the tolyl in both the cerium(III) complexes and their adducts were observed in the region 6.5-7.3 ppm as multiplet. The chemical shift for methyl (–CH<sub>3</sub>) protons of the neopentyl moiety appeared in the region 1.0-1.1 ppm while the chemical shift for methylene (–CH<sub>2</sub>) protons appeared in the region 3.9-4.4 ppm. These chemical shift values did not indicate any significant shift comparative to the parent dithiophosphate ligands. The addition complexes also exhibited peaks for the aromatic protons signals from the additional base ligands.

### ***<sup>31</sup>P NMR spectra***

In these mixed ligand complexes two separate singlets for the ditolyldithiophosphate and the neopentylenedithiophosphate were observed. The signal for the ditolyldithiophosphate and neopentylenedithiophosphate moieties appears in the regions 91.2-94.8 ppm and 80.8-83.4 ppm, respectively. Occurrence of two singlets for both the dithiophosphate moieties is suggestive of formation of mixed ditolyldithiophosphate-neopentylenedithiophosphate complexes. Furthermore, occurrence of a downfield shift (14–20 ppm) in comparison to the parent dithiophosphate ligands is indicative of the bidentate mode of linkage of both the dithiophosphate ligands with cerium. A deshielding of this extent has been interpreted by different researchers to be consistent with the bidentate behavior of the dithiophosphate groups indicating the bidentate nature of the dithiophosphate ligand [16,18]. The <sup>31</sup>P NMR spectra of the addition complexes with triphenylphosphine as the donor ligand exhibited the signal for the phosphorus atom of the triphenylphosphine moiety as a singlet in the region -4.8 to -4.9 ppm.

### ***<sup>13</sup>C NMR spectra***

The <sup>13</sup>C NMR spectra of few representative compounds (in CDCl<sub>3</sub>) have been recorded, which show that the chemical shifts due to the carbon of tolyl rings were found retained with a marginal shift in their values compared to the parent ligand. The chemical shift for the methyl (–CH<sub>3</sub>) carbon, attached to tolyl ring, was

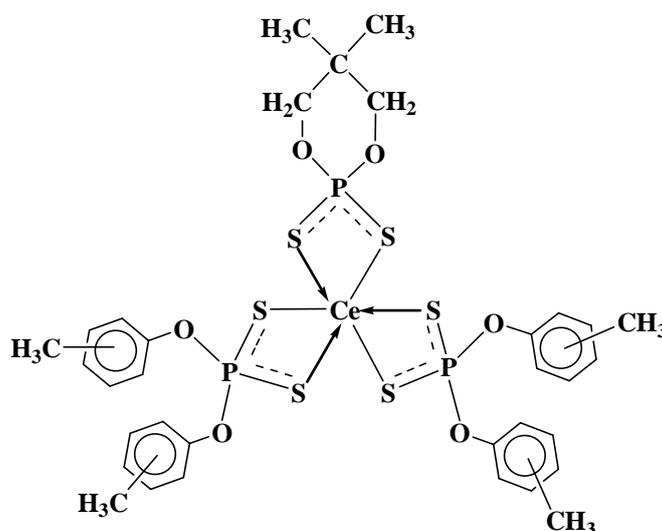
found in the region 16.4-20.5 ppm. The carbon nuclei of the aryl groups have displayed their resonance in the region 111.3-153.9 ppm. The chemical shifts for C–O carbon of *O,O*-tris-(*m*- or *p*-ditolyl)dithiophosphato derivatives were found in the region 151.5-154.6 ppm, which, perhaps, is due to the presence of intramolecular hydrogen bonding between proton attached to one of the *ortho* carbon of one tolyl ring and oxygen atom –O(C) of the other tolyl ring. This may be correlated with the probability of intramolecular hydrogen bonding in the these derivatives [30]. The  $^{13}\text{C}$  NMR spectra for the mixed ligand complexes depicted that the methyl (–CH<sub>3</sub>) carbon of the neopentylenedithiophosphate moiety resonates at 21.8-22.2 ppm, the methylene (–CH<sub>2</sub>–) carbon appears at 75.0-75.3 ppm and the quaternary carbon atom ( $\text{C}^{\text{q}}$ ) resonates at 32.5-32.8 ppm. The  $^{13}\text{C}$  NMR spectra of the addition complexes exhibited the signals of the carbon nuclei of the donor moieties in addition to the characteristic chemical shifts indicated above. In the addition complexes, the aryl carbon nuclei of the triphenylphosphine moiety resonated at 131.2-135.2 ppm.

### Mass spectra

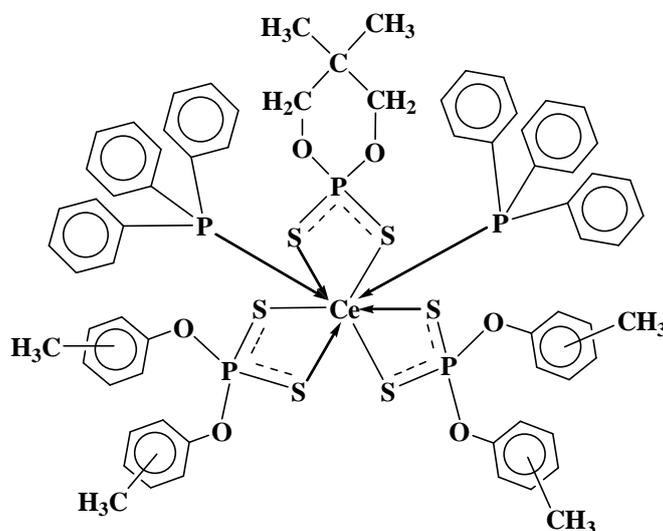
The mass spectra of two representative cerium(III) complexes represented molecular ion peak [M<sup>+</sup>] at 1066.8 (m/z) (**1a**) and 1591.4 (m/z) respectively. In addition to molecular ion peak several other peaks of different fragments were observed, which were formed after consecutive dismissal of different groups. The occurrence of molecular ion peak in the complexes is supporting the monomeric nature of the complexes.

### Structural Features

Literature survey [12-16,18] and observations based on elemental analysis, IR, NMR ( $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$ ) and mass spectral studies indicated that the dithiophosphates surround the cerium atom in the probable structure can be assigned to these complexes in figure 1-2. The in the (P)–O–C, P–O–(C), P=S and P–S bands for dithiophosphate moiety in comparison to the parent dithiophosphate ligands indicates the formation of these complexes. Further, the appearance of new bands was observed in the IR spectra of these complexes in comparison to the parent dithiophosphate ligands. A new band ascribed to  $\nu\text{Ce-S}$  (339.7-334.5 cm<sup>-1</sup>) is indicative of formation of cerium-sulfur bond in these complexes. A singlet for the phosphorus atom of the dithiophosphato moiety indicates the bidentate mode of chelation by dithiophosphate ligand in addition to the equivalent nature of the phosphorus atom in these complexes. Two singlets, for each phosphorus atom of the ditolyldithiophosphate and the neopentylenedithiophosphate moiety indicated the formation of the mixed ligand complexes. Therefore, hexacoordinate and octacoordinate geometries may tentatively be proposed around the cerium(III) atom in the complexes (**1-3**) (Figure 1) and the addition complexes (**4-6**) (Figure 2), respectively.



**Figure 1: Proposed six coordinate geometry for the mixed ligand dithiophosphate complexes of Cerium(III).**



**Figure2: Proposed eight coordinate geometry for the triphenyl adducts of mixed ligand dithiophosphate complexes of Cerium(III).**

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