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# Synthesis, crystal structures, luminescence properties and catalytic application of lanthanide(III) piperidine dithiocarbamate complexes



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#### ABSTRACT

A series of lanthanide(III) piperidine dithiocarbamate complexes [Ln(Pip-Dtc)<sub>3</sub>(Phen)] [where Ln = La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III), Er(III); Pip-Dtc = piperidine dithiocarbamate and Phen = 1,10-phenanthroline] has been synthesized and structurally characterized by analytical and various spectral techniques such as FT-IR, UV–Vis and <sup>1</sup>H NMR. The molecular structure of  $[Pr(Pip-Dtc)_3(Phen)]$ ,  $[Nd(Pip-Dtc)_3(Phen)]$  and  $[Sm(Pip-Dtc)_3(Phen)]$  complexes were determined by single crystal X-ray diffraction studies. The binding of the Pip-Dtc to the metal center involves two sulfur atoms and Phen through two nitrogen atoms. The metal center is octa-coordinated by three Pip-Dtc and one Phen ligands. The coordination geometry around Ln(III) ion is distorted dodecahedron. The photoluminescence properties of Sm(III), Pr(III), Tb(III), Dy(III) complexes indicated that the emission intensity depend on the nature of the metal ion, ligand and polarity of the medium. These complexes exhibited good to excellent catalytic activity in trimethylsilyl cyanation of benzaldehyde.

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# 1. Introduction

During recent past, considerable attention has been paid to the study of luminescence properties of lanthanide(III) ions because these ions have potential applications in various fields such as diagnostic values as luminescence probes [1,2], optical signal amplifier in telecommunication network [3,4] etc. For example Eu(III) and Tb(III) ions possess good luminescence characteristics based on the electronic transitions between the 4f energy levels, a series of compounds activated by these ions have been investigated for practical applications as phosphors [5,6]. Lanthanide(III) complexes with organic ligands often show strong luminescence due to the efficient energy transfer from the ligands to the rare earth ions. So there has been a growing interest in the studies of the luminescence properties of lanthanide(III) complexes with variety of organic ligands such as carboxylic acids [7],  $\beta$ -diketones [8], heterocyclic [9] ligands etc.

Dithiocarbamates are the soft sulfur donor ligands, lanthanide complex with dithiocarbamate was first reported by Jørgensen [10] in 1960s. Recent studies on lanthanide dithiocarbamate complexes focus mainly on their thermal properties because of their potential application as precursors for the fabrication of lanthanide sulfide nanoparticles [11], and thin films [12] and also as a catalyst for the synthesis of cyanohydrins [13]. More recently, room temperature luminescence study on the lanthanide(III) complexes which are structurally very close to the ones presented in this article has also been reported [14]. Hence, the main objective of the present work is the synthesis, crystal structure determination and preliminary luminescence studies on lanthanide(III) complexes of piperidine dithiocarbamate ligand. The catalytic activity of these complexes in cyanosilylation of benzaldehyde has also been investigated as cyanohydrins are well known natural products and versatile synthons in organic synthesis [15].

# 2. Experimental

#### 2.1. General information and physical measurements

Lanthanide metal salts LnCl<sub>3</sub>·6H<sub>2</sub>O and 1,10-phnanthroline were of commercially available high purity grade (Aldrich, India) and were used as received. Solvents were dried by standard procedures and other chemicals were used as received. Elemental analyses (CHNS) were carried out on Elementar Vario EL III at Sophisticated Analytical Instrumentation Facility, Cochin University of Science and Technology, Kochi. FT-IR spectra were recorded on a JASCO, Japan (460 plus) FT-IR spectrometer with KBr pellets in the range 4000–400 cm<sup>-1</sup>. Electronic absorption



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spectra of the complexes were recorded on a JASCO, Japan (V-630) double beam spectrophotometer with chloroform solvent. <sup>1</sup>H NMR spectra were recorded at Madurai Kamaraj University, Madurai in a Bruker, Switzerland NMR spectrometer (300 MHz, DMSO-d<sub>6</sub>).

Room temperature luminescence measurements were conducted using a JASCO, Japan (FP 6200) spectroflurimeter with 10 nm slit width and at a scan speed of 500 nm/min. Solutions for the study were of  $10^{-3}$  M or otherwise mentioned. Electrochemical experiments were performed with an electrochemical workstation CHI Instrument (643B, Austin, USA) under dry nitrogen. Tetrabutylammonium perchlorate (0.1 M) was used as the supporting electrolyte. A three-electrode configuration was employed with a platinum working electrode, a calomel electrode as a reference electrode and a platinum wire as auxiliary electrode.

Single crystal X-ray diffraction data for the complexes were collected at the University of Malaya, Kuala Lumpur, Malaysia on a Bruker APEX-II CCD area-detector with Mo K $\alpha$  radiation (k = 0.71073 Å) by the w scan mode. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes. Crystal structure refinements were carried using SHELXTL Ver. 6.12 W95/98/NT/2000/ME.

#### 2.2. Synthesis of the ligand

The ligand piperidine dithiocarbamate sodium salt (Pip-Dtc) has been synthesized using reported method with slight modification [16]. In a typical experiment sodium hydroxide (0.05 mol) was dissolved in 3 mL of water in an ice bath and 30 mL of ethanol was added to it. The solution was stirred with the addition of piperidine (0.05 mol), followed by drop by drop addition of carbon disulfide (0.05 mol) which yielded the precipitate of the dithiocarbamate sodium salt. The yellow product was collected by filtration, re-dissolved in minimum amount of methanol and the pure white product was precipitated by adding required volume of diethyl ether. Anal. Calc. for C<sub>6</sub>H<sub>10</sub>NS<sub>2</sub>Na: C, 39.32; H, 5.50; N, 7.64; S, 34.99. Found: C, 40.50; H, 5.20; N, 7.62; S, 34.90%. FT-IR (KBr pellet, cm<sup>-1</sup>): vC-N, 1467s; vC-S, 1002s, 967s. <sup>1</sup>H NMR ( $\delta$  ppm): (Fig. S1) 1.36 (m, 4H), 1.51 (m, 2H), 4.25 (t, J = 5.4 Hz, 4H). UV–Vis (nm, log  $\varepsilon$ ): 232 (4.00); 264 (4.35). Yield 85%.

#### 2.3. Preparation of Ln(III) complexes

The general method adopted for the preparation of the Ln(III) complexes (1-9) is shown in Scheme 1. A solution of Pip-Dtc (1.5 mmol) and Phen (0.5 mmol) in 10 mL methanol was added to a solution of corresponding hydrated lanthanide chloride (0.5 mmol) in 5 mL methanol. The mixture was stirred for few minutes during which the solid complex gets precipitated. Then the solid was isolated through vacuum filtration, washed with methanol and recrystalized from hot acetonitrile. The analytical and spectral characterizations of the complexes are:

#### 2.3.1. [La(Pip-Dtc)<sub>3</sub>(Phen)] (**1**)

White solid *Anal.* Calc. for  $C_{30}H_{38}LaN_5S_6$ : C, 45.04; H, 4.79; N, 8.75; S, 24.05. Found: C, 44.93; H, 5.00; N, 8.63; S, 23.90%. FT-IR (KBr pellet, cm<sup>-1</sup>): *v*C–N, 1480s; *v*C–S, 1008s; *v*(Phen), 1621, 1587, 1513, 850, 728. UV–Vis (nm, log  $\varepsilon$ ): 232 (2.46); 264 (3.21). <sup>1</sup>H-NMR ( $\delta$  ppm): (Fig. S2) 1.42 (d, *J* = 6 Hz, 12H), 1.56 (d,

*J* = 4.8 Hz, 6H), 4.18 (d, *J* = 4.2 Hz, 12H), 7.85 (s, 2H), 8.05 (s, 2H), 8.57 (d, *J* = 6.3 Hz, 2H), 9.24 (s, 2H). Yield 80%.

#### 2.3.2. $[Ce(Pip-Dtc)_3(Phen)]$ (2)

Brown solid *Anal.* Calc. for  $C_{30}H_{38}CeN_5S_6$ : C, 44.97; H, 4.78; N, 8.74; S, 24.01. Found: C, 44.90; H, 5.04; N, 8.51; S, 24.05%. FT-IR (KBr pellet, cm<sup>-1</sup>): *v*C–N, 1472s; *v*C–S, 975s; *v*(Phen), 1628, 1509, 1352, 852, 722. UV–Vis (nm, log  $\varepsilon$ ): 232 (4.46); 264 (4.90). Yield 90%.

#### 2.3.3. [Pr(Pip-Dtc)<sub>3</sub>(Phen)] (3)

Light mint green solid *Anal.* Calc. for  $C_{30}H_{38}PrN_5S_6$ : C, 44.93; H, 4.78; N, 8.73; S, 23.99. Found: C, 45.00; H, 5.12; N, 8.78; S, 23.90%. FT-IR (KBr pellet, cm<sup>-1</sup>):  $\nu$ C–N, 1473s;  $\nu$ C–S, 977s;  $\nu$ (Phen), 1623, 1513, 1344, 848, 728. <sup>1</sup>H NMR ( $\delta$  ppm): (Fig. S3) 0.46 (s, 12H), 0.95 (s, 6H), 3.16 (d, *J* = 6 Hz, 12H), 7.73 (s, 2H), 7.99 (s, 2H), 8.51 (s, 2H), 9.07 (s, 2H). UV–Vis (nm, log  $\varepsilon$ ): 232 (4.64); 264 (4.72). Yield 95%.

#### 2.3.4. [Nd(Pip-Dtc)<sub>3</sub>(Phen)] (4)

Pale purple solid *Anal.* Calc. for  $C_{30}H_{38}NdN_5S_6$ : C, 44.74; H, 4.76; N, 8.70; S, 23.89. Found: C, 44.60; H, 4.84; N, 8.68; S, 23.82%. FT-IR (KBr pellet, cm<sup>-1</sup>): *v*C–N, 1473s; *v*C–S, 997s; *v*(Phen), 1623, 1515, 1454, 1359, 983, 887, 728. <sup>1</sup>H NMR ( $\delta$  ppm): (Fig. S4) 1.12 (s, 12H), 1.41(s, 6H), 3.83 (s, 12H), 7.79 (s, 2H), 8.02 (s, 2H), 8.51 (s, 2H), 9.11 (s, 2H). UV–Vis (nm, log  $\varepsilon$ ): 232 (4.73); 264 (4.84). Yield 97%.

#### 2.3.5. $[Sm(Pip-Dtc)_3(Phen)]$ (5)

Light yellow solid *Anal.* Calc. for  $C_{30}H_{38}SmN_5S_6$ : C, 44.41; H, 4.72; N, 8.63; S, 23.71. Found: C, 44.23; H, 5.10; N, 8.60; S, 23.75%. FT-IR (KBr pellet, cm<sup>-1</sup>): *v*C–N, 1473s; *v*C–S, 985s; *v*(Phen), 1623, 1517, 1423, 1359, 948, 885, 728. <sup>1</sup>H NMR ( $\delta$  ppm): (Fig. S5) 1.39 (d, *J* = 3 Hz, 12H), 1.53 (d, *J* = 3 Hz, 6H), 4.11 (s,12H), 7.77 (m, 2H), 8.02 (s, 2H), 8.51(d, *J* = 9 Hz, 2H), 9.09 (d, *J* = 6 Hz, 2H), UV–Vis (nm, log  $\varepsilon$ ): 232 (4.83); 264 (4.98). Yield 98%.

#### 2.3.6. [Gd(Pip-Dtc)<sub>3</sub>(Phen)] (**6**)

White solid Anal. Calc. for  $C_{30}H_{38}GdN_5S_6$ : C, 44.03; H, 4.68; N, 8.56; S, 23.51. Found: C, 44.24; H, 5.23; N, 8.60; S, 23.15%. FT-IR (KBr pellet, cm<sup>-1</sup>): *v*C–N, 1474s; *v*C–S, 988s; *v*(Phen), 1622, 1517, 1424, 1350, 883, 722. UV–Vis (nm, log  $\varepsilon$ ): 232 (5.23); 264 (6.78). Yield 85%.

#### 2.3.7. [Tb(Pip-Dtc)<sub>3</sub>(Phen)] (7)

White solid Anal. Calc. for  $C_{30}H_{38}TbN_5S_6$ : C, 43.94; H, 4.67; N, 8.54; S, 23.46. Found: C, 44.24; H, 5.23; N, 8.60; S, 23.15%. FT-IR (KBr pellet, cm<sup>-1</sup>): vC-N, 1475s; vC-S, 989s; v(Phen), 1625, 1513, 1425, 1351, 1229, 1111, 883, 722. UV-Vis (nm, log  $\varepsilon$ ): 232 (5.63); 264 (6.88). Yield 87%.

#### 2.3.8. [Dy(Pip-Dtc)<sub>3</sub>(Phen)] (8)

Light yellow solid *Anal.* Calc. for  $C_{30}H_{38}DyN_5S_6$ : C, 44.75; H, 4.65; N, 8.50; S, 23.36. Found: C, 44.25; H, 4.63; N, 8.54; S, 23.35%. FT-IR (KBr pellet, cm<sup>-1</sup>):  $\nu$ C–N, 1475s;  $\nu$ C–S, 990s;  $\nu$ (Phen), 1623, 1512, 1426, 1351, 1229, 1112, 884, 723. UV–Vis (nm, log  $\varepsilon$ ): 232 (5.73); 264 (6.67). Yield 92%.

#### 2.3.9. [Er(Pip-Dtc)<sub>3</sub>(Phen)] (9)

Pale pink solid *Anal.* Calc. for  $C_{30}H_{38}ErN_5S_6$ : C, 43.50; H, 4.62; N, 8.46; S, 23.23. Found: C, 44.01; H, 4.53; N, 8.34; S, 23.34%. FT-IR (KBr pellet, cm<sup>-1</sup>): *v*C–N, 1475s; *v*C–S, 990s; *v*(Phen), 1623, 1512, 1426, 1351, 1229, 1112, 884, 723. UV–Vis (nm, log  $\varepsilon$ ): 232 (5.73); 264 (6.67). Yield 96%.



Scheme 1. Preparation of the [Ln(Pip-Dtc)<sub>3</sub>(Phen)] complexes.

## 3. Results and discussion

The [Ln(Pip-Dtc)<sub>3</sub>(Phen)] complexes (where Ln = La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III), Er(III)) were synthesized (Scheme 1) and characterized using conventional analytical and spectroscopic techniques such as FT-IR, UV–Vis and <sup>1</sup>H NMR. The crystal structures of [Pr(Pip-Dtc)<sub>3</sub>(Phen)]·CHCl<sub>3</sub> (**3**), [Nd(Pip-Dtc)<sub>3</sub>(Phen)]·CHCl<sub>3</sub> (**4**) and [Sm(Pip-Dtc)<sub>3</sub>(Phen)]·CHCl<sub>3</sub> (**5**) were determined and discussed. Molar conductance of the complexes was measured in chloroform and the values obtained between 0 and 0.0012 S m<sup>2</sup> Mol<sup>-1</sup> are consistent with their non electrolytic nature. Luminescence properties of selected complexes are also investigated and discussed. The catalytic activity of these complexes in trimethylsilylcyanation of carbonyl compound is also screened.

#### 3.1. Crystal structures

The single crystals of the complexes **3**, **4** and **5** were prepared by the solvent diffusion method using chloroform and diethyl ether as

the solvents. The crystal structures of the complexes **3**, **4** and **5** are shown in Figs. 1–3, respectively, and the crystallographic data are given in Table 1. Selected bond angles and bond lengths are collected in Table 2. The results indicated that the complexes **3**, **4** and **5** are isostructural i.e. octa-coordinated. It is evident from these figures that, the geometry of the crystals are distorted dodecahedron around the Ln(III) ion. There are three dithiocarbamate ligands coordinated through six sulfur atoms and a Phen ligand coordinated through two nitrogen atoms.

The average Ln–S bond distances are 2.9002(1), 2.876(2) and 2.851(1) Å in **3**, **4** and **5**, respectively. The average Ln–N bond distances are 2.669(3), 2.642(3) and 2.615 Å in **3**, **4** and **5**, respectively. These average bond distances are very close to the observed average values reported previously [13b]. The average Ln–S and Ln–N bond distance of these complexes showed a gradual decrease in the order Pr(III) > Nd(III) > Sm(III). These observations are consistent with the fact that ionic radius of the lanthanide metal ions decreases from left to right along the period due to the lanthanide contraction which is also reflected in metal–ligand bond length of these complexes.



Fig. 1. Molecular structure of [Pr(Pip-Dtc)<sub>3</sub>(Phen)]·CHCl<sub>3</sub> (3).



Fig. 2. Molecular structure of [Nd(Pip-Dtc)<sub>3</sub>(Phen)]·CHCl<sub>3</sub> (4).



Fig. 3. Molecular structure of [Sm(Pip-Dtc)<sub>3</sub>(Phen)]·CHCl<sub>3</sub> (5).

The obtained results of the bond angles (°) of the three dithiocarbamate ligands, in these crystals, are interesting. The S–Ln–S bond angles for the two dithiocarbamate ligands, which are in equatorial position to the Phen ligand, are relatively higher than that of the third dithiocarbamate ligand which is present in the axial position to the Phen ligand. The opposite bite angles of the three dithiocarbamate ligands also exhibited similar trend i.e. S– C–S angles of the two equatorial ligands are higher than that of the axial ligand. The observed effect in the coordination sphere of the metal ion is obvious due to the structural constrains imposed by the bulky Phen ligand frame work.

The following general conclusions were drawn from the foregoing results. All the three compounds investigated crystallized in a triclinic system and their structural features are comparable with their analogues reported in the literature [17]. In these three complexes, the average length (Å) of C–S bond is 1.7138(4) which is significantly shorter than the C–S single bond length (1.81) and higher than the C=S distance (1.69). The observed intermediate

#### Table 1

Summary o	of crystallographic	data for the	complexes 3,	4 and 5.

Table	2			
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Selected bond	parameters	of complexes	<b>3</b> , <b>4</b> and <b>5</b> .
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(3)		(4)		<b>(5</b> )	
Bond lengths (Å)					
Pr1-S1	2.870(2)	Nd1-S1	2.840(2)	Sm1-S1	2.818(2)
Pr1-S2	2.866(1)	Nd1-S2	2.854(2)	Sm1-S2	2.830(2)
Pr1-S3	2.920(1)	Nd1-S3	2.876(2)	Sm1-S3	2.853(1)
Pr1-S4	2.934(1)	Nd1-S4	2.894(2)	Sm1-S4	2.863(2)
Pr1-S5	2.897(1)	Nd1-S5	2.884(2)	Sm1-S5	2.857(1)
Pr1-S6	2.914(1)	Nd1-S6	2.908(2)	Sm1-S6	2.885(1)
Pr1-N4	2.666(3)	Nd1-N1	2.633(3)	Sm1-N1	2.605(3)
Pr1-N5	2.672(3)	Nd1-N2	2.650(3)	Sm1-N2	2.624(3)
Bond angles	(°)				
S1-Pr1-S2	62.05(4)	S1-Nd1-S2	62.05(5)	S1-Sm1-S2	62.59(4)
S3-Pr1-S4	60.30(3)	S3-Nd1-S4	61.12(4)	S3-Sm1-S4	61.63(3)
S5-Pr1-S6	61.20(3)	S5-Nd1-S6	60.47(4)	S5-Sm1-S6	61.07(4)
N4-Pr1-	62.21(10)	N1-Nd1-	62.30(11)	N4-Sm1-	63.15(11)
N5		N2		N5	
Averages					
Bond length	s (Å)				
Pr-S	2.9002(1)	Nd-S	2.876(2)	Sm–S	2.851(1)
Pr–N	2.669(3)	Nd–N	2.642(3)	Sm–N	2.615(3)
C–S	1.7226(4)	C–S	1.7091(5)	C–S	1.7098(4)
Bond angles	(°)				
S-Pr-S	61.18(3)	S-Nd-S	61.21(3)	S-Sm-S	61.76(4)
S-C-S	117.90(2)	S-C-S	117.86(2)	S-C-S	117.73(3)

value between the C–S and C=S bond distances indicated that a partial double bond nature arises due to the chelated sulfur atoms [18]. The powder XDR patterns of the complexes **6** and **9** (as representative cases) for which we are not able to prepare single crystals are also recorded to have an insight into the structure of the complexes. The powder XRD patterns (Figs. S6 and S7) of these complexes are similar to that of **3**, **4** and **5** (generated from the single crystal data) indicating that these complexes possess the same structure viz. dodecahedron.

#### 3.2. Electronic absorption studies

As representative cases, the absorption spectra of complexes (**3**) and (**5**) were recorded in chloroform and are shown in Figs. 4 and 5, respectively. For the mixed-ligand complexes, the strong absorption bands situated in the UV region are centered at 232 and

Complex	(3)	(4)	(5)
Empirical Formula	$C_{31}H_{39}Cl_3N_5S_6Pr$	$C_{31}H_{39}Cl_3N_5S_6Nd$	C31H39Cl3N5 S6Sm
Formula Weight	921.29	924.62	930.73
Crystals system	Triclinic	Triclinic	Triclinic
Space group	ΡĪ	PĪ	ΡĪ
a (Å)	11.16740(10)	11.203(4)	11.1945(17)
b (Å)	11.85410(10)	11.952(5)	11.9391(18)
<i>c</i> (Å)	15.8966(2)	16.065(6)	16.047(3)
α (Å)	68.7360(10)	68.466(5)	68.423(2)
$\beta$ (Å)	83.1820(10)	82.647(6)	82.532(2)
γ (Å)	80.5860(10)	80.095(6)	79.898(2)
$V(Å^3)$	1930.66(3)	1966.3(13)	1958.4(5)
Ζ	2	2	2
Wavelength (Å)	0.71073	0.71073	0.71073
$D_{\text{calc}}$ (mg/m <sup>3</sup> )	1.585	1.562	1.578
Abs coefficient $(mm^{-1})$	1.824	1.872	2.053
Crystal size (mm <sup>3</sup> )	$0.35 \times 0.16 \times 0.10$	$0.41 \times 0.34 \times 0.28$	$0.42\times0.38\times0.24$
$\theta$ range (°)	1.38-25.00	2.38-25.74	2.22-25.94
Reflections collected	6762	7599	7580
Independent reflections	6388	6522	6671
Data/restraints/parameters	6388/0/415	6522/0/415	6671/0/415
F(000)	932	934	938
$R_1/wR_2$	0.0341/0.0845	0.0516/0.1048	0.0418/0.1013



Fig. 4. Electronic absorption spectrum of [Pr(Pip-Dtc)<sub>3</sub>(Phen)] in chloroform. The inset shows the f-f transitions of Pr(III) ion.



Fig. 5. Electronic absorption spectrum of  $[Sm(Pip-Dtc)_3(Phen)]$  in chloroform. The inset shows the f-f transitions of Sm(III) ion.

264 nm. The first band is attributed to the  $\pi \to \pi^*$  transitions of the bidentate aromatic Phen ligand. The very intense band at 264 nm is a result of the overlapping of absorption peaks of the aromatic Phen ligand and the N-CS<sub>2</sub> chromophore of the dithiocarbamate ligand. In the visible region, a number of very weak and narrow bands (characteristic of the Laporte-forbidden f–f transitions of the La(III) ions) are observed. In the present study, the band assignments were made by comparison with the spectra of the Ln(III) ions in halide lattices (LaCl<sub>3</sub> and LaF<sub>3</sub>) and with the spectra of the Ln(III) aquo ions in dilute acid solution [19].

For the Pr(III) complex, the observed f–f transition (inset in Fig. 4) corresponds to transitions from the ground state  ${}^{3}H_{4}$  to the excited states  ${}^{3}P_{2}$ ,  ${}^{1}I_{6}$ ,  ${}^{3}P_{1}$ ,  ${}^{3}P_{0}$  and  ${}^{1}D_{2}$ . It is interesting to note that the small but evident band that corresponds to the  ${}^{3}H_{4} \rightarrow {}^{1}I_{6}$  transition found in the spectrum of the Pr(III) complex is hardly observable in the spectrum of the Pr(III) aquo ion [20]. This particular transition is hypersensitive to the environment about the Pr(III) ion. On the other hand, the bands observed for the Sm(III)

Table 3	
Electronic absorption spectra	l data and relating bonding parameters.

Complexes	Ln(III) aqua ion (cm <sup>-1</sup> )	Complex (cm <sup>-1</sup> )	log ε	Covalent parameter
[Pr(Pip-Dtc) <sub>3</sub> (Phen)] <b>3</b> [Sm(Pip-Dtc) <sub>3</sub> (Phen)] <b>5</b>	22,547 - 21,367 20,768 16,997 24,968 24,067	21,881 21,030 20,790 20,100 16,542 23,980 23,310	2.03 1.69 1.73 1.49 1.45 2.28 1.90	$\beta = 0.9714  \delta\% = 2.9423  b^{1/2} = 0.1195  \beta = 0.9750  \delta\% = 2.5597  b^{1/2} = 0.447  b^{1/2} =$
	21,575 20,920	21,533 20,358	1.50 1.43	$b^{1/2} = 0.1117$

complex (inset in Fig. 5) are attributed to transitions from the ground state  ${}^{6}H_{5/2}$  to  $({}^{4}P_{5/2} + {}^{6}P_{5/2})$ ,  ${}^{4}M_{19/2}$ ,  ${}^{4}I_{13/2}$  and  $({}^{4}I_{9/2} + {}^{4}M_{15/2})$ states. The electronic spectra of the complexes showed a general red shift of the f-f spectral bands in comparison with those of their corresponding aquo ions. These red shifts are due to the nephelauxetic effect and are regarded as a measure of covalency of bonding between the metal ion and the ligands. The spectroscopic covalent parameters of the Ln(III)-ligand bonds, such as the nephelauxetic ratio  $\beta$ , Sinha's parameter  $\delta$ , and bonding parameter  $b^{1/2}$  were calculated and are collected in Table 3. The nephelauxetic ratio ( $\beta$ ) less than one and positive values of Sinha's parameter ( $\delta$ ) and bonding parameter ( $\hat{b}^{1/2}$ ) suggested the occurrence of some covalent character in the metal-ligand bond [21]. This may be due to the fact that the presence of the easily polarizable sulfur atoms allows one to expect covalent character between the soft ligand and the hard lanthanide(III) ions [22].

#### 3.3. FT-IR study

Since, the FT-IR spectra of all the complexes are similar, the important details of the FT-IR spectrum of  $[Pr(Pip-Dtc)_3(Phen)]$  is alone discussed here, as a representative case. The characteristic absorption of the hydroxyl group is not present in the complex, indicating that the complex does not contain any water molecule. The FT-IR spectrum of the free dithiocarbamate ligand exhibited a doublet at 1002 and 967 cm<sup>-1</sup> corresponds to vC-S stretching [23]. In the complex, it appeared as a singlet at 977 cm<sup>-1</sup> indicating

coordination of the ligand, in a bidentate manner, with the metal ion. The peak corresponds to vC–N stretching appeared at 1473 cm<sup>-1</sup> in the complex.

#### 3.4. <sup>1</sup>H NMR study

Though the complexes, except La(III), are paramagnetic in nature, some of the complexes (**2**, **3** and **4**) gave reliable <sup>1</sup>H NMR spectrum in DMSO-d<sub>6</sub> solvent (Figs. S2–S5). The spectral data are collected in the experimental section. For the free Pip-Dtc ligand there are three peaks appeared at 1.36 (m, 4H), 1.51 (m, 2H) and 4.25 (t, J = 5.4 Hz, 4H) ppm correspond to ten aliphatic protons. In these complexes, there are three Pip-Dtc ligands having thirty aliphatic protons which give three peaks as they are in three different environments. Only one Phen ligand is present in the complex, which has eight protons in four different environments, giving four peaks. In the complexes, the observed broadening of the peaks may be due to the paramagnetic nature of the complexes and/or significant electron delocalization between metal and ligands [24].

#### 3.5. Luminescence studies

As representative cases the luminescence spectra of Pr(III), Sm(III), Tb(III) and Dy(III) complexes were investigated at room temperature and the spectra obtained are shown in Fig. 6. It is evident from the Figure that the most intense emission was observed for the Dy(III) and Sm(III) complexes and also they emit with nearly equal intensities. The Tb(III) complex emits with medium intensity and the Pr(III) complex exhibited a weak red luminescence.

The room temperature excitation and emission spectra of the Pr(III) complex (**3**) are shown in Fig. 7. The 610 nm emission line was monitored to obtain the excitation spectrum, which consists of an intense ligand-centered transition band and several weak peaks corresponding to f–f transitions of Pr(III). The emission spectrum was recorded using 362 nm excitation which showed three peaks. The intense peak centered at 610 nm is mainly from the  ${}^{1}D_{2} \rightarrow {}^{3}H_{4}$  transition, but it is also believed to be overlapping with a much weaker peak corresponding to the  ${}^{3}P_{0} \rightarrow {}^{3}H_{6}$  transition. The very weak emission peaks at 548 and 663 nm correspond to transitions from the  ${}^{3}P_{0}$  emissive state to the  ${}^{3}H_{5}$  and  ${}^{3}F_{2}$  levels, respectively. Regulacio et al. [14] have reported that the excited states  ${}^{1}I_{6}$ ,  ${}^{3}P_{1}$ ,  ${}^{3}P_{0}$  and  ${}^{1}D_{2}$  of Pr(III) are close in energy to the Phen-centered



**Fig. 6.** Emission spectra of  $[Ln(Pip-Dtc)_3(Phen)]$  complexes in acetonitrile at room temperature. (Excitation wavelengths are Pr(III), 362; Sm(III), 316; Tb(III), 260; Dy(III), 290 nm).



Fig. 7. Excitation and emission spectra of  $[Pr(Pip-Dtc)_3(Phen)]$  complex (3) in acetonitrile at room temperature. (Excitation 362 nm; Emission 610 nm; concentration  $1\times 10^{-3}$  M).

triplet state and the energy transfer to lower emissive state  ${}^{1}G_{4}$  is not efficient since it is located far below the Phen-localized triplet state of the complex. In most of the Pr(III) complexes emission originates mainly from the  ${}^{3}P_{0}$  and  ${}^{1}D_{2}$  levels and the nonradiative relaxations from the  ${}^{1}I_{6}$  and  ${}^{3}P_{1}$  states to the lower energy levels. Voloshin et al. [25] have reported that the emission properties of organic chelates of Pr(III) can be controlled depending on the position of the ligand triplet state relative to the  ${}^{3}P_{0}$  and  ${}^{1}D_{2}$  emitting levels. For the complex (**3**), the most intense emission comes from the  ${}^{1}D_{2}$  level with very weak emission originating from the  ${}^{3}P_{0}$ state. Weak peaks corresponding to intra-configurational f–f transitions from the ground-state of Pr(III) are also observed in the spectrum.

The room temperature excitation and emission spectra of the Sm(III) complex (**5**) are shown in Fig. 8. The excitation spectrum was obtained by monitoring the 600 nm line of the  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$  emission. It contains a very intense broadband that corresponds to the excitation of the organic chromophore (S<sub>0</sub>  $\rightarrow$  S<sub>1</sub>). Several



Fig. 8. Excitation and emission spectra of  $[Sm(Pip-Dtc)_3(Phen)]$  complex (5) in acetonitrile at room temperature. (Excitation 316 nm; Emission 600 nm; concentration  $1.25\times10^{-3}$  M).

weak peaks corresponding to f-f transitions from the ground state of Sm(III) are also seen. There are three emission peaks originate from the Sm(III) lowest emitting state  ${}^{4}G_{5/2}$  and correspond to transitions to  ${}^6H_{9/2}$  (563 nm),  ${}^6H_{7/2}$  (600 nm), and  ${}^6H_{5/2}$  (645 nm) levels. The fourth peak, which is the least intense peak, corresponds to transition from a higher emissive state  ${}^{4}F_{3/2}$  to the ground state <sup>6</sup>H<sub>5/2</sub> (545 nm). The bright luminescence observed for the Sm(III) complex is reflective of a good match between the ligand-centered triplet state and the Sm(III) emissive states. For the Sm(III) ion the excited states that can receive energy from the lowest triplet state of ligand are  ${}^4G_{7/5}$ ,  ${}^4F_{3/2}$  and  ${}^4G_{5/2}$ . In the present study, in the Sm(III) complex the intense emission observed corresponds to  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$  (600 nm). According to Zheng et al. [26] this is due to the close proximity of these three excited states to each other, which causes electrons from the higher states to rapidly relax to the <sup>4</sup>G<sub>5/2</sub> level, from where radiative transitions occur.

The excitation and emission spectra of the Tb(III) and Dy(III) are shown in Figs. S8 and S9, respectively. The Tb(III) complex exhibited four peaks at 482, 535, 584 and 645 nm as a result of emission from  ${}^5D_4$  to the  ${}^7F_6$ ,  ${}^7F_5$ ,  ${}^7F_4$  and  ${}^7F_3$  states, respectively. Among them  ${}^5D_4 \rightarrow {}^7F_4$  (584 nm) is very intense one. For Dy(III) complex there are two emission peaks are appeared at 480 and 582 nm. The higher intensity emission arises from the transition  ${}^4F_{9/2}$  to  ${}^6H_{13/2}$  (582 nm) and the lower intensity peak arises due to the transition from  ${}^4F_{9/2}$  to  ${}^6H_{15/2}$  (480 nm).

In the case of Tb(III) and Pr(III) complexes the ligands sensitize the lanthanide ions less efficiently and as a result their emission peaks are less intense when compared to those in the case of Sm(III) and Dy(III) complexes. The lack of bright emission observed for the Tb(III) and Pr(III) complexes can also be due to the poor match between the lowest ligand-centered triplet state and the Tb(III) and Pr(III) main emissive states.

With an aim to investigate the effect of ligands on the emissive property of the complexes the room temperature emission study was carried out by replacing 1,10-phenanthroline by a bidentate aromatic lignad bipyridine (Bipy) in Sm(III) complex as a representative case. It is evident from the Fig. S10 that [Sm(Pip-Dtc)<sub>3</sub>Phen] gives intense emission spectrum than [Sm(Pip-Dtc)<sub>3</sub>Bipy] and thus Phen acts as an efficient antenna rather than Bipy ligand. Likewise, the piperidine dithiocarbmate (Pip-Dtc) also replaced by other two dithiocarbamate ligands viz., azepane dithiocarbamate (Aze-Dtc)



Fig. 9. Role of solvents on the emission of [Sm(Pip-Dtc)<sub>3</sub>(Phen)] complex (excitation at 316 nm; concentration  $1\times 10^{-3}$  M) (a) H<sub>2</sub>O (b) CH<sub>3</sub>CN (c) CHCl<sub>3</sub> (d) CH<sub>2</sub>Cl<sub>2</sub> (In water the complex was sonicated and used).

[13b] and pyrrolidine dithiocarbamate (Pyrrol-Dtc) [13c] in the Sm(III) complex. In these cases the order of emission was observed to be Pyrrol-Dtc > Aze-Dtc > Pip-Dtc also without a shift in emission maximum (Fig. S11). The effect of solvent on the luminescence property is also studied with [Sm(Pip-Dtc)<sub>3</sub>Phen] complex as a representative case. The emission spectra recorded in acetonitrile, chloroform, dichloromethane and water are given in Fig. 9. It is clear that the solvent polarity also plays a vital role in the emission intensity of the lanthanide(III) complexes. The results indicated that the emission intensity increased with an increase in polarity of the solvent i.e. the order of emission observed is  $H_2O > CH_3CN > CH_2Cl_2$ .

Based on the results and discussion on the emission studies of the Ln(III) complexes the following general conclusions were drawn. (i) The ligands effectively sensitize samarium and dysprosium complexes when compared to praseodymium and terbium complexes and the order of emission is Dy(III)  $\approx$  Sm(III) > Tb(III) > Pr(III); (ii) 1,10-Phenanthroline acts as an efficient antenna than bipyridine; (iii) The emission intensity was observed to increase with an increase in solvent polarity and (iv) Pyrrolidine dithiocarbamate ligand gives relatively a higher emission than piperidine and azepane dithiocarbamates.

#### 3.6. Electrochemical properties

Solution electrochemical behaviors of the ligand and a representative complex, [Sm(Pip-Dtc)<sub>3</sub>(Phen)], in 0.1 M [Bu<sub>4</sub>N][ClO<sub>4</sub>]/ CH<sub>2</sub>Cl<sub>2</sub> solution were investigated. The cyclic voltammograms recorded at a scan rate of 20 mVs<sup>-1</sup> is shown in Fig. 10. The voltammogram of the ligand Pip-Dtc exhibited one oxidation peak at 0.201 V and two reduction peaks at -0.834 and -1.434 V. The [Sm(Pip-Dtc)<sub>3</sub>(Phen)] complex also exhibited similar CV curves with one oxidation peak at 0.328 V and two reduction peaks at -0.982 and -1.524 V. Since the oxidation state of the central trivalent lanthanide ion does not change, the electrochemical behavior observed in this complex is due to successive removal or addition of electrons from or to the ligand-based orbitals [27]. The observed results indicated that the oxidation potential of Pip-Dtc ligand showed a significant shift in the complex when compared to the free ligand. The oxidation potential in the complex is more positive than that in the free ligand which suggested that the oxidation of



Fig. 10. Cyclic voltammagram of (a)  $[Sm(Pip-Dtc)_3(Phen)]$  (pink) (b) Pip-Dtc (blue) in 0.1 M  $[Bu_4N][ClO_4]/DCM$  at a scan rate of 20 mVs<sup>-1</sup>. (Color online.)



Scheme 2. Catalytic activity.

Table 4

Percentage yields of the products obtained in the trimethylsilylcyanation reaction.

_	Complex	DCM, yield (%)	THF, yield (%)
	[La(Pip-Dtc) <sub>3</sub> (Phen)]	80	97
	[Ce(Pip-Dtc) <sub>3</sub> (Phen)]	79	86
	[Pr(Pip-Dtc) <sub>3</sub> (Phen)]	90	98
	[Nd(Pip-Dtc) <sub>3</sub> (Phen)]	87	95
	[Sm(Pip-Dtc) <sub>3</sub> (Phen)]	85	96
	[Gd(Pip-Dtc) <sub>3</sub> (Phen)]	82	84
	[Tb(Pip-Dtc) <sub>3</sub> (Phen)]	78	89
	[Dy(Pip-Dtc) <sub>3</sub> (Phen)]	75	85
	[Er(Pip-Dtc) <sub>3</sub> (Phen)]	92	97

The consumption of benzaldehyde was observed by TLC. Yields refer to the isolated products.

Pip-Dtc ligand in the complex is relatively difficult. This may be due to the fact that the ligand donates electrons in forming coordinate bonds with the metal ion that makes the oxidation difficult.

## 4. Catalytic activity

The usefulness of these complexes as a catalyst in trimethylsilylcvanation of a carbonyl compound has been investigated in dicholoromethane and tetrahydrofuran solvents. In a typical experiment, to a stirred solution of 1 mol% [Ln(Pip-Dtc)<sub>3</sub>(Phen)] in a given solvent, 0.5 mL (4.9 mmol) of benzaldehyde was added at room temperature under nitrogen atmosphere. Then 1.1 mL (8.79 mmol) of trimethylsilyl cyanide was added to the reaction mixture and the same was stirred for 6 h under inert atmosphere. After completion of the reaction, the reaction mixture was quenched with water and extracted with *n*-hexane/ethyl acetate 2:8 (v/v). The organic layer was dried over sodium sulfate and concentrated. The crude material was purified by column chromatography by using 3–5% of ethyl acetate in pet-ether to give pure product as a colorless liquid. The product was characterized using <sup>1</sup>H NMR spectra (Fig. S12). The overall reaction is shown in Scheme 2 and the percentage yields obtained are collected in Table 4.

Brunel and Holmes [28] have reviewed the development of chemically catalyzed asymmetric cyanohydrin syntheses. Many metal ions like Ti(IV), V(IV), Sn(II), Mg(II), Al(III), etc. and few lanthanide La(III), Yb(III), Sm(III) salts/complexes were found to catalyze the cyanation of aldehydes and ketones to give cyanohydrins. They concluded that, in the case of lanthanide catalyzed reactions, catalysts loading of 10 mol% were routinely used and at the same time lanthanide derived systems are proving to be a very fruitful area of research. Recently, Vale et al. [29] have reported the use of lanthanide-dithiocarbamate complexes as catalyst in such reaction giving 65–98% yield of the product. However, the time required was reported to be 6–11 h. In the present study, the results indicated that the good to excellent yields obtained, with 1 mol% catalyst in 6 h at RT, is comparable with those reported using transition metal and lanthanide complexes as

catalyst [30]. The advantages of the present complexes are the simple preparation method with relatively good yields, anhydrous nature of the complexes and free solubility of the complexes in common organic solvents.

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#### Appendix A. Supplementary data

CCDC 871335, 880710 and 880711 contain the supplementary crystallographic data for 3, 4 and 5, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2015.03.012.

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