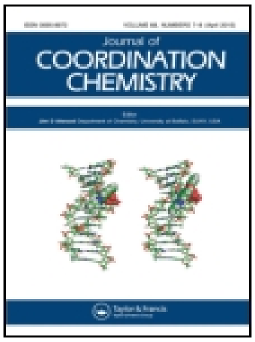

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# Synthesis, spectral characterization, crystal structures of lanthanide(III) pyrrolidine dithiocarbamate complexes and their catalytic activity

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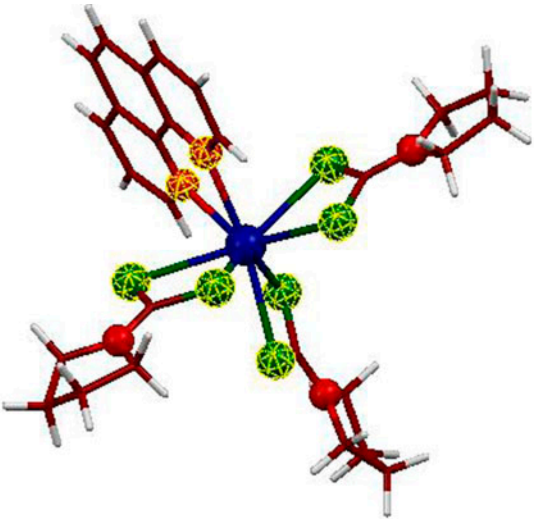

A series of lanthanide(III) pyrrolidine dithiocarbamate complexes [Ln(Pyrrol-Dtc)$_3$(Phen)] {Pyrrol-Dtc = pyrrolidine dithiocarbamate; Phen = 1,10-phenanthroline; Ln = La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III), Er(III)} have been synthesized and structurally characterized. The molecular structures of [La(Pyrrol-Dtc)$_3$(Phen)], [Pr(Pyrrol-Dtc)$_3$(Phen)], [Sm(Pyrrol-Dtc)$_3$(Phen)], and [Dy(Pyrrol-Dtc)$_3$(Phen)] have been confirmed using single crystal XRD studies. The results reveal that in these complexes, the central Ln(III) ion is coordinated to three Pyrrol-Dtc and one Phen and possesses a distorted dodecahedron geometry. Catalytic activity of these complexes in trimethylsilylcyanation reaction has been studied.

*Keywords*: Lanthanide; Pyrrolidine dithiocarbamate; 1,10-phenanthroline; Crystal structure

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## 1. Introduction

Lanthanide complexes have been of considerable interest because of their potential applications in fluorescent labeling reagents, imaging agents, emitter materials in organic light emitting diodes, luminescent probes, and sensory materials [1–7]. During attempts to prepare these complexes for various applications, organic ligands having oxygen and/or nitrogen donors have been utilized in the sensitization of lanthanide ions, in particular, aromatic amines, carboxylic acids, and β-diketones provide efficient energy transfer to lanthanide ions [8–10]. However, very little has been reported on the luminescence of lanthanide ions coordinated to sulfur donors [11]. To investigate the less studied luminescence properties of lanthanide complexes containing sulfur ligands, we, in the present endeavor, have synthesized nine lanthanide(III) pyrrolidine dithiocarbamate complexes, [Ln(Pyrrol-Dtc)$_3$(Phen)], where Ln = La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III), and Er(III) under mild reaction conditions. The complexes were characterized using conventional analytical techniques such as elemental analysis, UV–vis, FT-IR, and $^1$H NMR spectral studies. The single crystal X-ray structures of [La(Pyrrol-Dtc)$_3$(Phen)], [Pr(Pyrrol-Dtc)$_3$(Phen)], [Sm(Pyrrol-Dtc)$_3$(Phen)], and [Dy(Pyrrol-Dtc)$_3$(Phen)] are reported and discussed. The photoluminescence properties of Pr(III), Sm(III), Tb(III), and Dy(III) complexes were studied at room temperature. The catalytic activities of these complexes in cyanosilylation of benzaldehyde are also reported.

## 2. Experimental

### 2.1. *General information and physical measurements*

The pyrrolidine dithiocarbamate ammonium salt (Pyrrol-Dtc) was purchased from Merck, India, and used as received. The lanthanide metal salts, LnCl$_3$·6H$_2$O, and 1,10-phenanthroline were purchased from Aldrich, India, and used as received. Solvents for spectral measurements were of commercially available spectral grades and are used as received. Elemental analyses (CHNS) were carried out on an Elementar Vario EL III at the Sophisticated Test and Instrumentation Center at Cochin University of Science and Technology, Kochi. FT-IR spectra were recorded on a JASCO, Japan (460 plus), FT-IR spectrometer with KBr pellets from 4000 to 400 cm$^{-1}$. Electronic absorption spectra of the complexes were recorded on a JASCO, Japan (V-630) double beam spectrophotometer in chloroform. $^1$H NMR spectra were recorded at Madurai Kamaraj University, Madurai, in a Bruker, Switzerland, NMR spectrometer (300 MHz). Room temperature luminescence measurements were conducted using a JASCO, Japan (FP 6200), spectrofluorimeter with 10 nm slit width and a scan speed of 500 nm min$^{-1}$.

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 ω 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 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 out using SHELXTL Ver. 6.12 W95/98/NT/2000/ME.

## 2.2. *General procedure for the synthesis of 1–9*

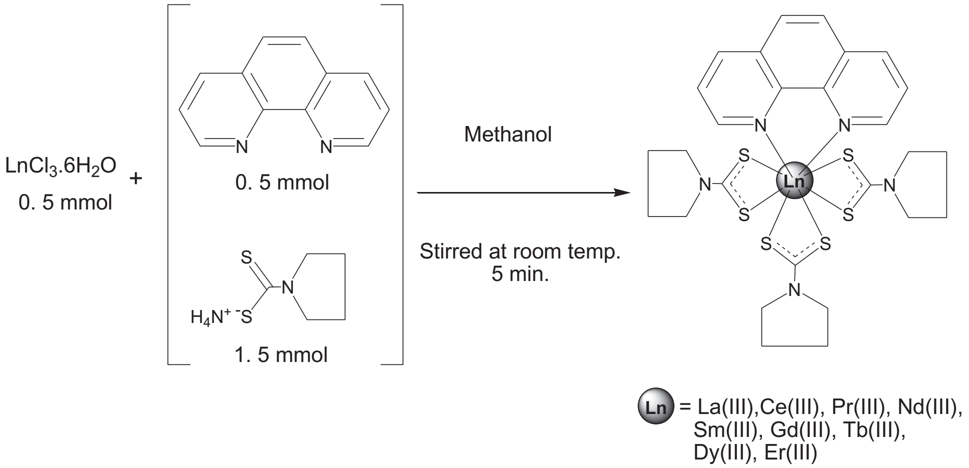
The method adopted for synthesis of these complexes is shown in scheme 1. In a typical experiment, a solution of Pyrrol-Dtc (1.5 mmol) and Phen (0.5 mmol) in 10 mL methanol was added to a solution of $LnCl_3 \cdot 6H_2O$ (0.5 mmol) in 5 mL methanol. The reaction mixture was stirred for 5 min, and the crystalline solid product that came out was isolated through vacuum filtration and washed several times with methanol. The Ln(III) complexes were characterized using elemental analyses, UV–vis, FT-IR, and $^1$H NMR techniques, and the results thus obtained are given.

For X-ray diffraction studies, single crystals were grown by adopting the following procedure. Approximately 500 mg of complex is dissolved in 20 mL of chloroform in a vial which is kept in an airtight bottle containing 100 mL diethyl ether. After slow vapor diffusion of diethyl ether into the chloroform solution, X-ray quality single crystals were obtained.

**2.2.1. [La(Pyrrol-Dtc)$_3$(Phen)] (1).** Pale yellow solid analyzed for $C_{27}H_{32}LaN_5S_6$, Calcd (%): C, 42.79; H, 4.26; N, 9.24; S, 25.39. Found (%): C, 41.93; H, 4.00; N, 8.93; S, 24.90; FT-IR (KBr pellet, cm$^{-1}$): *ν*C–N, 1421s; *ν*C–S, 1002s; *ν*(Phen), 1619, 1587, 1513, 1160, 852, 730. UV–vis (nm, log *ε*): 266, 2.63; $^1$H-NMR (*δ* ppm): (figure S1, see online supplemental material at http://dx.doi.org/10.1080/00958972.2015.1037299) 1.84 (d, $J = 6.3$ Hz, 12H), 3.65 (d, $J = 6.6$ Hz, 12H), 7.82 (d, $J = 4.2$ Hz, 2H), 8.03 (s, 2H), 8.53 (d, $J = 7.8$ Hz, 2H), 9.17 (s, 2H); Yield 85%.

**2.2.2. [Ce(Pyrrol-Dtc)$_3$(Phen)] (2).** Brown solid isolated was analyzed for $C_{27}H_{32}CeN_5S_6$, Calcd (%): C, 42.72; H, 4.25; N, 9.23; S, 25.35. Found (%): C, 41.90; H, 4.50; N, 8.95; S, 24.95; FT-IR (KBr pellet, cm$^{-1}$): *ν*C–N, 1423s; *ν*C–S, 1004s; *ν*(Phen), 1621, 1513, 1326, 1109, 914, 850, 719; UV–vis (nm, log *ε*): 265, 2.92; Yield 92%.

**2.2.3. [Pr(Pyrrol-Dtc)$_3$(Phen)] (3).** Light mint green solid isolated was analyzed for $C_{27}H_{32}PrN_5S_6$, Calcd (%): C, 42.68; H, 4.24; N, 9.22; S, 25.32%. Found (%): C, 43.00; H,



Scheme 1. Preparation of [Ln(Pyrrol-Dtc)$_3$(Phen)].

4.12; N, 8.98; S, 24.90; FT-IR (KBr pellet, cm$^{-1}$): *v*C–N, 1421s; *v*C–S, 1004s; *v*(Phen), 1621, 1513, 1326, 1160, 912, 852, 719; $^1$H NMR (*δ* ppm): (figure S2) 1.03 (s, 12H), 2.08 (s, 12H), 7.75 (s, 2H), 7.97 (s, 2H), 8.47 (d, *J* = 6.2 Hz, 2H), 9.09 (s, 2H); UV–vis (nm, log *ε*): 266, 2.82; Yield 95%.

**2.2.4. [Nd(Pyrrol-Dtc)$_3$(Phen)] (4).** Pale purple product isolated was analyzed for $C_{27}H_{32}NdN_5S_6$, Calcd (%): C, 42.49; H, 4.23; N, 9.18; S, 25.21%. Found (%): C, 42.60; H, 4.84; N, 8.98; S, 25.52; FT-IR (KBr pellet, cm$^{-1}$): *v*C–N, 1419s; *v*C–S, 1002s; *v*(Phen), 1623, 1590, 1513, 1419, 1344, 943, 862, 727; $^1$H NMR (*δ* ppm): (figure S3) 1.02 (s, 12H), 2.05 (s, 12H), 7.79 (s, 2H), 7.99 (s, 2H), 8.45 (s, 2H), 9.06 (s, 2H); UV–vis (nm, log *ε*): 266, 2.87; Yield 97%.

**2.2.5. [Sm(Pyrrol-Dtc)$_3$(Phen)] (5).** Pale yellow solid isolated was analyzed for $C_{27}H_{32}SmN_5S_6$, Calcd (%): C, 42.15; H, 4.19; N, 9.10; S, 25.01%. Found (%): C, 42.23; H, 4.18; N, 9.60; S, 24.75; FT-IR (KBr pellet, cm$^{-1}$): *v*C–N, 1421s; *v*C–S, 1006 s; *v*(Phen), 1621, 1513, 1326, 946, 852, 730; $^1$H NMR (*δ* ppm): (figure S4) 1.78 (d, *J* = 3.6 Hz, 12H), 3.54 (s,12H), 7.79 (d, *J* = 4.2 Hz, 2H), 8.01 (s, 2H), 8.50 (d, *J* = 8.1 Hz, 2H), 9.10 (d, *J* = 2.1 Hz, 2H); UV–vis (nm, log *ε*): 266, 2.68; Yield 88%.

**2.2.6. [Gd(Pyrrol-Dtc)$_3$(Phen)] (6).** White solid obtained was analyzed for $C_{27}H_{32}GdN_5S_6$, Calcd (%): C, 41.78; H, 4.16; N, 9.02; S, 24.79%. Found (%): C, 42.24; H, 4.23; N, 9.60; S, 24.15; FT-IR (KBr pellet, cm$^{-1}$): *v*C–N, 1421s; *v*C–S, 1008s; *v*(Phen), 1621, 1515, 1461, 1326, 1160, 946, 852, 721; UV–vis (nm, log *ε*): 266, 2.78; Yield 85%.

**2.2.7. [Tb(Pyrrol-Dtc)$_3$(Phen)] (7).** White solid obtained was analyzed for $C_{27}H_{32}TbN_5S_6$, Calcd (%): C, 41.69; H, 4.15; N, 9.00; S, 24.73%. Found (%): C, 41.24; H, 4.23; N, 8.90; S, 24.15; FT-IR (KBr pellet, cm$^{-1}$): *v*C–N, 1421s; *v*C–S, 1008s; *v*(Phen), 1621, 1515, 1326, 1216, 1159, 946, 852, 721; UV–vis (nm, log *ε*): 266, 3.08; Yield 87%.

**2.2.8. [Dy(Pyrrol-Dtc)$_3$(Phen)] (8).** Pale yellow solid isolated was analyzed for $C_{27}H_{32}DyN_5S_6$, Calcd (%): C, 41.50; H, 4.13; N, 8.96; S, 24.62. Found (%): C, 41.25; H, 4.63; N, 8.74; S, 24.35; FT-IR (KBr pellet, cm$^{-1}$): *v*C–N, 1421s; *v*C–S, 1010s; *v*(Phen), 1623, 1515, 1326, 1216, 948, 862, 721; UV–vis (nm, log *ε*): 267, 3.67; Yield 92%.

**2.2.9. [Er(Pyrrol-Dtc)$_3$(Phen)] (9).** Pale pink solid isolated was analyzed for $C_{27}H_{32}ErN_5S_6$, Calcd (%): C, 41.25; H, 4.10; N, 8.91; S, 24.47. Found (%): C, 41.01; H, 4.53; N, 8.34; S, 23.84; FT-IR (KBr pellet, cm$^{-1}$): *v*C–N, 1475s; *v*C–S, 990s; *v*(Phen), 1623, 1512, 1426, 1351, 1229, 1112, 884, 723; UV–vis (nm, log *ε*): 266, 3.67; Yield 96%.

## 3. Results and discussion

The [Ln(Pyrrol-Dtc)$_3$(Phen)] complexes were synthesized and characterized using conventional analytical and spectroscopic techniques. The crystal structures of

[La(Pyrrol-Dtc)$_3$(Phen)] (**1**), [Pr(Pyrrol-Dtc)$_3$(Phen)] (**3**), [Sm(Pyrrol-Dtc)$_3$(Phen)] (**5**), and [Dy(Pyrrol-Dtc)$_3$(Phen)].CHCl$_3$ (**8**) were determined to confirm the structure of the complexes. The catalytic activities of all the complexes in trimethylsilylcyanation of benzaldehyde were also investigated and discussed.

### 3.1. *Crystal structures*

The crystal structure of **1** is shown in figure 1 (as a representative case) and that of **3**, **5**, and **8** are shown in figures S5–S7, respectively. The crystallographic data are given in table 1. Selected bond lengths and angles are collected in table 2. All the complexes are isostructural with their metal analogs. It is evident from the crystallographic data that the geometry of the complexes is a distorted dodecahedron around Ln(III). In these complexes, there are three dithiocarbamate ligands coordinated through six sulfurs and a Phen coordinated through two nitrogens. The compounds crystallize in the triclinic *P-1* space group and average Ln–S and Ln–N bond distances in **1** of 2.9509(5) and 2.6908(15) Å in **3**, 2.9101(5) and 2.6484(16) Å, in **5**, 2.8701(8) and 2.5955(3) Å, and in **8**, 2.8360(6) and 2.530(2) Å, respectively. The average Ln–S and Ln–N bond distances of these complexes showed a gradual decrease in the order La(III) > Pr(III) > Sm(III) > Dy(III) and these

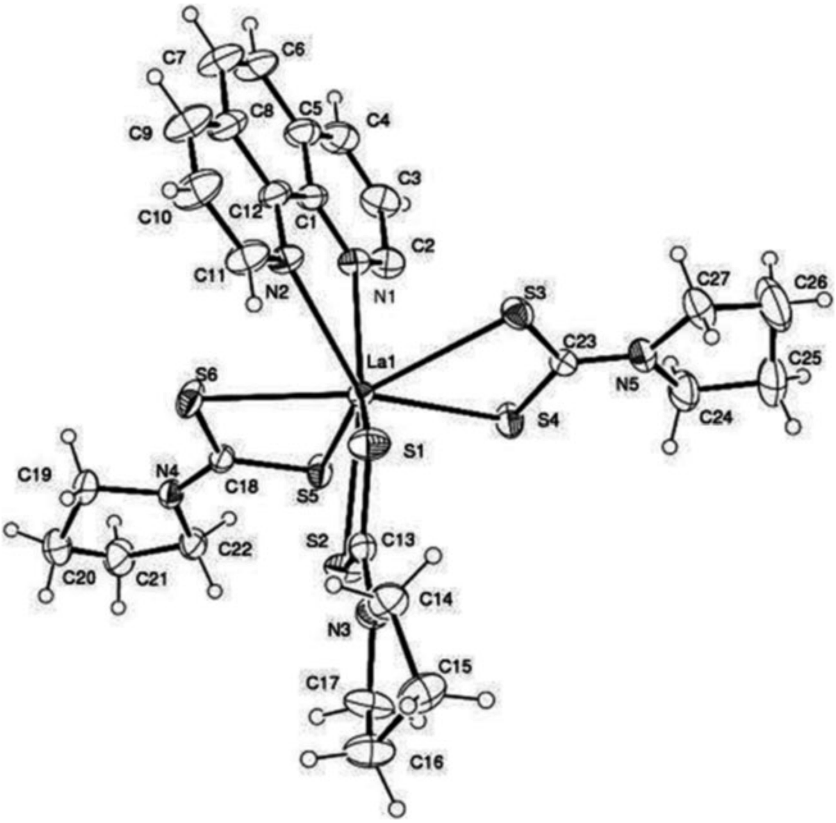


Figure 1. Molecular structure of [La(Pyrrol-Dtc)$_3$(Phen)] (**1**).

Table 1. Summary of crystallographic data for **1**, **3**, **5**, and **8**.

| Complex | **1** | **3** | **5** | **8** |
|---|---|---|---|---|
| Empirical formula | $C_{27}H_{32}N_5S_6La$ | $C_{27}H_{32}N_5S_6Pr$ | $C_{27}H_{32}N_5S_6Sm$ | $C_{28}H_{33}Cl_3N_5S_6Dy$ |
| Formula weight | 757.82 | 759.85 | 763.25 | 900.80 |
| Crystal system | Triclinic | Triclinic | Triclinic | Triclinic |
| Space group | P-1 | P-1 | P-1 | P-1 |
| $a$ (Å) | 10.3216(3) | 10.2405(3) | 9.9835(2) | 10.25670(10) |
| $b$ (Å) | 10.5061(3) | 10.4832(3) | 10.4169(2) | 10.2854(2) |
| $c$ (Å) | 17.2105(7) | 17.1983(5) | 17.2104(3) | 17.1442(2) |
| $\alpha$ (Å) | 97.082(2) | 96.8630(10) | 96.7560(10) | 83.3750(10) |
| $\beta$ (Å) | 102.929(2) | 102.8170(10) | 102.6690(10) | 88.4910(10) |
| $\gamma$ (Å) | 113.7480(10) | 113.5330(10) | 112.8460(10) | 74.5910(10) |
| Volume (Å$^3$) | 1616.63(9) | 1605.23(8) | 1567.80(5) | 1731.94(4) |
| $Z$ | 2 | 2 | 2 | 2 |
| Wavelength (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Density (calc) (mg/m$^3$) | 1.555 | 1.572 | 1.617 | 1.727 |
| Abs. coefficient (mm$^{-1}$) | 1.734 | 1.934 | 2.297 | 2.779 |
| Crystal size (mm$^3$) | 0.30 × 0.25 × 0.20 | 0.20 × 0.10 × 0.10 | 0.24 × 0.21 × 0.15 | 0.24 × 0.10 × 0.08 |
| $\theta$ range (deg) | 2.23–31.82 | 2.25–31.81 | 2.00–30.54 | 2.38–28.43 |
| Reflections collected | 12,113 | 5660 | 6460 | 6422 |
| Independent reflections | 10,312 | 5378 | 6057 | 6032 |
| Data/restraints/parameters | 10,312/10/410 | 5378/27/391 | 6057/1/346 | 6032/0/388 |
| $F$(0 0 0) | 762 | 768 | 764 | 898 |
| R1/wR2 | 0.0363/0.0654 | 0.0179/ 0.0406 | 0.0252/0.0712 | 0.0219/0.0547 |

observations are consistent with the fact that ionic radii of the lanthanide ions decrease from left to right along the period due to the lanthanide contraction. The S–Ln–S bond angles (°) of the 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. Similar trend was exhibited for S–C–S bite angles also. The crystal structures investigated are comparable with their analogs [12–14]. The average bond length (Å) of C–S bond in these complexes is 1.72, 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 value between the single bond (C–S) and the double bond (C=S) distances showed a partial double bond nature of the S═C═S bonds [15].

### 3.2. *Electronic absorption spectral study*

As a representative case, electronic absorption spectrum of [Pr(Pyrrol-Dtc)$_3$(Phen)] was recorded in chloroform and is shown in figure 2(a). For the mixed-ligand complex, there are two absorption bands in the UV region at 238 and 267 nm. The first band (shorter wavelength band) in the spectrum is attributed to the $\pi \rightarrow \pi^*$ transition of the bidentate aromatic ligand. The very intense band at 267 nm is a result of overlapping absorption peaks of the aromatic ligands and the NCS$_2$ chromophore of the dithiocarbamate [12]. In the visible region, weak and narrow peaks characteristic of the Laporte-forbidden f–f transitions of the lanthanide ions are observed [figure 2(b)]. The peak assignments were made by comparison with spectra of the Ln(III) ions in halide lattices ($LaCl_3$ and $LaF_3$) and with the spectrum of the Ln(III) aquo ions in dilute acid solution [16, 17]. The observed f-f transition for [Pr(Pyrrol-Dtc)$_3$(Phen)] is given in figure 2(b) and that of [Nd(Pyrrol-Dtc)$_3$(Phen)] and [Sm(Pyrrol-Dtc)$_3$(Phen)] are given in figures S8 and S9, respectively. For the Pr(III) ion, the observed f–f transition takes place from the ground state $^3H_4$ to the excited states

Table 2. Selected bond parameters of **1**, **3**, **5**, and **8**.

| **1** | | **3** | | **5** | | **8** | |
|---|---|---|---|---|---|---|---|
| *Bond lengths (Å)* | | | | | | | |
| La1–S1 | 2.9796(5) | Pr1–S1 | 2.9209(6) | Sm1–S1 | 2.8551(9) | Dy1–S1 | 2.8977(6) |
| La1–S2 | 2.9253(5) | Pr1–S2 | 2.8771(5) | Sm1–S2 | 2.9045(9) | Dy1–S2 | 2.8091(7) |
| La1–S3 | 2.9907(5) | Pr1–S3 | 2.8929(5) | Sm1–S3 | 2.8428(8) | Dy1–S3 | 2.8542(7) |
| La1–S4 | 2.9323(5) | Pr1–S4 | 2.9494(5) | Sm1–S4 | 2.8972(9) | Dy1–S4 | 2.8190(7) |
| La1–S5 | 2.9171(5) | Pr1–S5 | 2.9351(6) | Sm1–S5 | 2.8368(8) | Dy1–S5 | 2.7926(7) |
| La1–S6 | 2.9607(5) | Pr1–S6 | 2.8855(6) | Sm1–S6 | 2.8845(9) | Dy1–S6 | 2.8439(7) |
| La1–N1 | 2.6949(15) | Pr1–N4 | 2.6506(17) | Sm1–N4 | 2.590(3) | Dy1–N4 | 2.547(2) |
| La1–N2 | 2.6867(15) | Pr1–N5 | 2.6461(16) | Sm1–N5 | 2.601(3) | Dy1–N5 | 2.513(2) |
| *Bond angles (°)* | | | | | | | |
| S1–La1–S2 | 60.373(14) | S1–Pr1–S2 | 61.622(15) | S1–Sm1–S2 | 62.36(2) | S1–Dy1–S2 | 62.990(18) |
| S3–La1–S4 | 60.290(14) | S3–Pr1–S4 | 61.127(15) | S3–Sm1–S4 | 62.31(2) | S3–Dy1–S4 | 63.046(19) |
| S5–La1–S6 | 60.832(13) | S5–Pr1–S6 | 61.117(16) | S5–Sm1–S6 | 62.66(2) | S5–Dy1–S6 | 63.112(19) |
| N1–La1–N2 | 61.31(5) | N4–Pr1–N5 | 62.26(5) | N4–Sm1–N5 | 63.71(9) | N4–Dy1–N5 | 65.62(7) |
| *A*verages | | | | | | | |
| *Bond lengths (Å)* | | | | | | | |
| La–S | 2.9509(5) | Pr–S | 2.9101(5) | Sm–S | 2.8701(8) | Dy–S | 2.8360(6) |
| La–N | 2.6908(15) | Pr–N | 2,6484(16) | Sm–N | 2.5955(3) | Dy–N | 2.530(2) |
| C–S | 1.7106(18) | C–S | 1.7118(2) | C–S | 1.7186(3) | C–S | 1.7206(3) |
| *Bond angles (°)* | | | | | | | |
| S–La–S | 60.4966(2) | S–Pr–S | 61.2886(15) | S–Sm–S | 62.4433(3) | S–Dy–S | 63.0493(18) |
| S–C–S | 120.7333(1) | S–C–S | 120.1466(11) | S–C–S | 119.9333(2) | S–C–S | 119.08(16) |

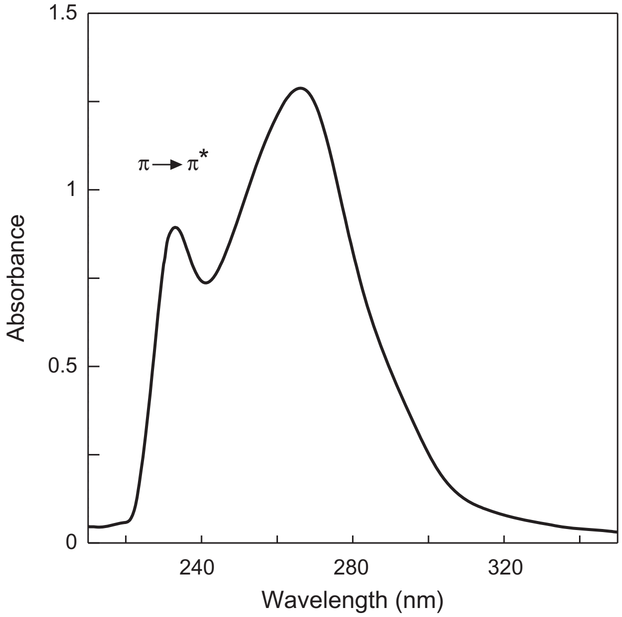


Figure 2a. Electronic absorption spectrum of [Pr(Pyrrol-Dtc)$_3$(Phen)].

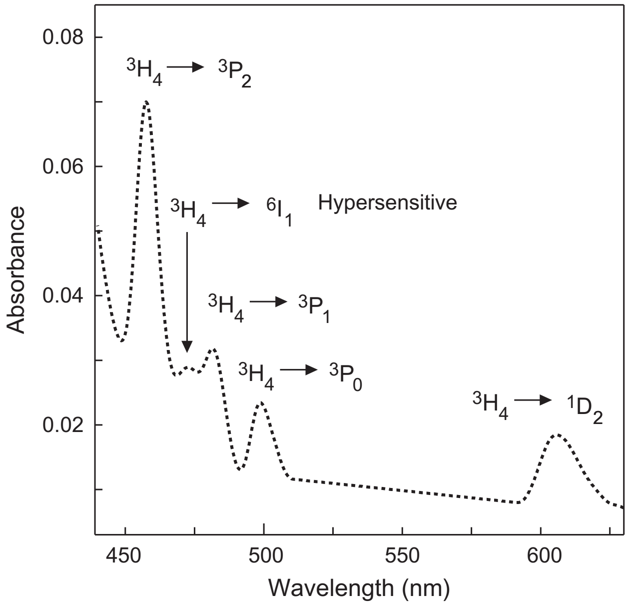


Figure 2b. Electronic f-f transition of [Pr(Pyrrol-Dtc)$_3$(Phen)] in visible region.

$^3P_2$, $^1I_6$, $^3P_1$, and $^3P_0$. The small but evident peak that corresponds to the $^3H_4 \rightarrow {}^1I_6$ transition in the spectrum of the Pr(III) complex is hardly observable in the spectrum of the Pr(III) aquo ion. This particular transition is hypersensitive to the environment about the Pr(III) ion [11, 12, 18, 19].

The presence of the easily polarizable sulfur donors allows one to expect more covalent character between the soft ligand and the hard lanthanide ions. The nature of the red shift may be used as a measure of the metal ligand covalent bonding. The electronic spectra of the Ln(III) complexes showed a general red shift of all the f–f spectral bands in comparison with those of their corresponding aquo ions (table 3). These red shifts are due to the nephelauxetic effect which is a measure of the covalency of the metal–ligand bonding. The spectroscopic covalent parameters of the metal–ligand bonds in these complexes were calculated and are also collected in table 3. A nephelauxetic ratio ($\beta$) of less than one and positive values of Sinha's parameter ($\delta$%) and the bonding parameter ($b^{1/2}$) suggest some covalent character in the metal–ligand bond. Also, the magnitudes of the bonding parameter ($b^{1/2}$) and Sinha's parameter ($\delta$%) decrease from Pr(III) to Sm(III), indicating that the extent of the covalent character of the metal–ligand bond decreases with increasing atomic number of the metal ion, consistent with the observation made by us [12] and by Su *et al.* [19, 20].

### 3.3. *FT-IR spectral study*

Since FT-IR spectra of all the complexes are similar, only the details of the FT-IR spectrum of [Pr(Pyrrol-Dtc)$_3$(Phen)] are 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 water. The FT-IR spectrum of the free dithiocarbamate exhibited a doublet

Table 3. Electronic absorption spectral data and bonding parameters.

| Complexes | Ln(III) aqua ion ($cm^{-1}$) | Complex ($cm^{-1}$) | Red shift ($cm^{-1}$) | Covalent parameter |
|---|---|---|---|---|
| [Pr(Pyrrol-Dtc)$_3$(Phen)] | 22,548 | 21,858 | 690 | |
| | | 21,164 | – | $\delta\% = 3.1145$ |
| | 21,368 | 20,768 | 599 | $\beta = 0.9698$ |
| | 20,768 | 20,060 | 708 | $b^{1/2} = 0.1229$ |
| | 16,992 | 16,515 | 477 | |
| [Nd(Pyrrol-Dtc)$_3$(Phen)] | 21,053 | 20,920 | 133 | |
| | 19,194 | 18,949 | 245 | $\delta\% = 1.8676$ |
| | 17,406 | 16,938 | 469 | $\beta = 0.9817$ |
| | 14,728 | 14,298 | 430 | $b^{1/2} = 0.0927$ |
| | 13,514 | 13,346 | 168 | |
| | 12,602 | 12,325 | 277 | |
| [Sm(Pyrrol-Dtc)$_3$(Phen)] | 24,969 | 24,753 | 216 | |
| | 24,067 | 23,960 | 107 | $\delta\% = 0.4090$ |
| | 21,575 | 21,552 | 23 | $\beta = 0.9959$ |
| | 20,921 | 20,877 | 44 | $b^{1/2} = 0.0422$ |

at 998 and 989 $cm^{-1}$ corresponding to $\nu$(CSS) [21]. In the complex, it appeared as a singlet at 1004 $cm^{-1}$, indicating bidentate coordination of the ligand. The peaks of Phen are also present in the spectrum of the complex.

**3.4. $^1$H NMR spectral study.** All the complexes under investigation are paramagnetic (except **1**); though the complexes are paramagnetic, some of the complexes gave reliable $^1$H NMR spectra in DMSO-d$_6$. The $^1$H NMR spectra of [La(Pyrrol-Dtc)$_3$(Phen)], [Pr(Pyrrol-Dtc)$_3$(Phen)], [Nd(Pyrrol-Dtc)$_3$(Phen)], and [Sm(Pyrrol-Dtc)$_3$(Phen)] were recorded in DMSO-d$_6$ and are shown in figures S1–S4; the spectral data are collected in the Experimental section. The $^1$H NMR spectra of these complexes exhibited two peaks in the aliphatic region, one at 1.8 ppm as a doublet for 12 protons and another at 3.6 ppm, also a doublet for another twelve protons, corresponding to the protons of the pyrrolidine rings present in the dithiocarbamate ligands. In the aromatic region, there are four peaks between 7.75 and 9.17 ppm that correspond to the protons of Phen. In spectra of the complexes, the peaks are slightly broader when compared to that of the free ligand, perhaps due to significant electron delocalization between metal ion and the ligands [22].

### 3.5. *Luminescence study*

The room temperature emission spectral studies of [Pr(Pyrrol-Dtc)$_3$(Phen)], [Sm(Pyrrol-Dtc)$_3$(Phen)], [Tb(Pyrrol-Dtc)$_3$(Phen)], and [Dy(Pyrrol-Dtc)$_3$(Phen)] were carried out as representative cases. The emission spectrum of [Pr(Pyrrol-Dtc)$_3$(Phen)] recorded using the $S_0 \rightarrow S_1$ (325 nm) excitation is shown in figure 3. The emission spectrum consists of an intense ligand-centered transition and several weak peaks corresponding to f–f transitions of Pr(III). The intense peak centered at 610 nm is mainly from the $^1D_2 \rightarrow {}^3H_4$ transition, but it is also believed to be overlapping with a much weaker peak corresponding to the $^3P_0 \rightarrow {}^3H_6$ transition. The very weak emission peaks at 563 and 642 nm correspond to transitions from the $^3P_0$ emissive state to the $^3H_5$ and $^3F_2$ levels, respectively. Regulacio *et al.* have reported that the excited states $^1I_6$, $^3P_1$, $^3P_0$, and $^1D_2$ of Pr(III) are close in energy to the Phen-centered triplet state and the energy transfer to lower emissive state $^1G_4$ is not efficient since it is located far below the Phen-localized triplet state of the complex [11]. In most praseodymium complexes, emission originates mainly from the $^3P_0$ and $^1D_2$ levels and the nonradiative relaxations from the $^1I_6$ and $^3P_1$ states to the lower energy levels occur. Voloshin *et al.* have demonstrated 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 $^3P_0$ and $^1D_2$ emitting levels [23]. Thus, in the present study, in the case of [Pr(Pyrrol-Dtc)$_3$(Phen)] the most intense emission comes from the $^1D_2$ level and the very weak emission originates from the $^3P_0$ state.

As seen from figure 4, in the emission spectrum of [Sm(Pyrrol-Dtc)$_3$(Phen)], there are three emission peaks from the Sm(III) lowest emitting state $^4G_{5/2}$ corresponding to transitions to $^6H_{9/2}$ (645 nm), $^6H_{7/2}$ (600 nm), and $^6H_{5/2}$ (563 nm) levels. The fourth peak, which is the least intense peak, corresponds to transitions from a higher emissive state $^4F_{3/2}$ to the ground state $^6H_{5/2}$ (537 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 three excited states that can receive energy from the lowest triplet state of ligand are $^4G_{7/5}$, $^4F_{3/2}$, and $^4G_{5/2}$. However, the intense emission is observed only from the $^4G_{5/2}$ level. According to Zheng *et al.*, the close proximity of these three excited states to each other causes electrons from the higher states to rapidly relax to the $^4G_{5/2}$ level, from which radiative transitions occur [24]. Parallel to this observation, the Sm(III) complex, in the present study, gives emission peaks in which $^4G_{5/2} \rightarrow {}^6H_{7/2}$ (600 nm) emission is the most intense.

The emission spectra of [Tb(Pyrrol-Dtc)$_3$(Phen)] and [Dy(Pyrrol-Dtc)$_3$(Phen)] were also recorded and are shown in figures 5 and 6, respectively. The Tb(III) complex exhibited four peaks at 485, 548, 584, and 620 nm and are the result of emissions from $^5D_4$ to $^7F_6$, $^7F_5$,

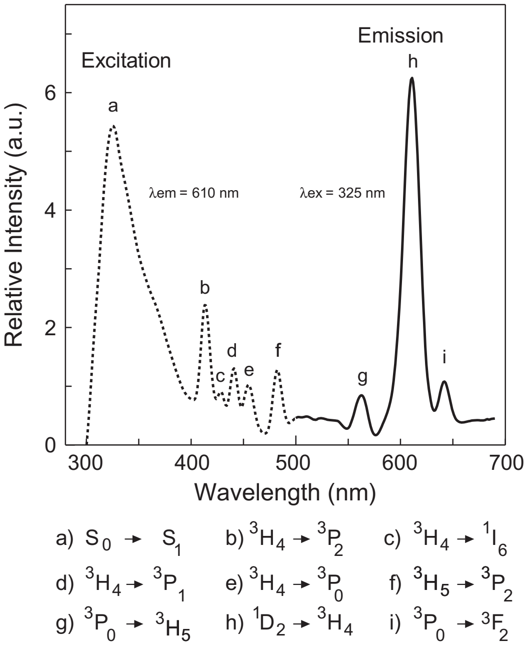


Figure 3. Emission spectrum of [Pr(Pyrrol-Dtc)$_3$(Phen)].

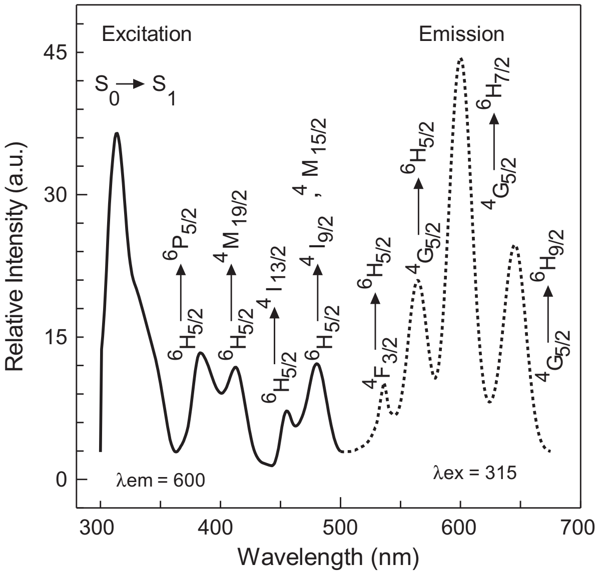


Figure 4. Emission spectrum of [Sm(Pyrrol-Dtc)$_3$(Phen)].

$^7F_4$, and $^7F_3$ states, respectively. Among them, $^5D_4 \rightarrow {}^7F_5$ (548 nm) is very intense. In the Dy(III) complex, there are two emission peaks at 480 and 575 nm and both are higher intensity emissions which arise due to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (480 nm) and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (575 nm) transitions. The results of the luminescence studies indicated that the ligands less efficiently sensitize the Tb(III) and Pr(III) complexes than their Sm(III) and Dy(III) counterparts, and as a result, their emission peaks are relatively less intense. The lack of bright emission observed for these compounds can also be explained by the poor match between the lowest ligand-centered triplet state and the Tb(III) and Pr(III) main emissive states.

### 3.6. *Catalytic activity*

Developments pertaining to the chemically catalyzed asymmetric cyanohydrin syntheses have been reviewed by Brunel and Holmes [25]. Salts and/or complexes of metals such as Ti(IV), V(IV), Sn(II), Mg(II), Al(III), *etc.* and those of a few lanthanides like La(III), Yb (III), and Sm(III) were found to catalyze the cyanation of aldehydes and ketones to give cyanohydrins. In the case of lanthanide catalyzed reactions, a catalyst loading of 10 mol% was routinely used; lanthanide derived systems are proving to be a very fruitful area of research. Recently, the use of lanthanide dithiocarbamate complexes as catalyst in such reaction giving good yields of the product was demonstrated by us [12] and by Vale *et al.* [26, 27].

In continuation of such reactions, the catalytic activity of Ln(III) complexes, reported in the present study, in trimethylsilylcyanation of benzaldehyde was investigated in dichloromethane and tetrahydrofuran. In a typical experiment, to a stirred solution of 1 mol% [Ln(Pyrrol-Dtc)$_3$(Phen)] in a given solvent, 0.5 mL of benzaldehyde was added at room temperature under nitrogen. Then, 1.1 mL of trimethylsilyl cyanide was added to the reaction mixture and stirred for 6 h under inert atmosphere. After completion of the reaction,

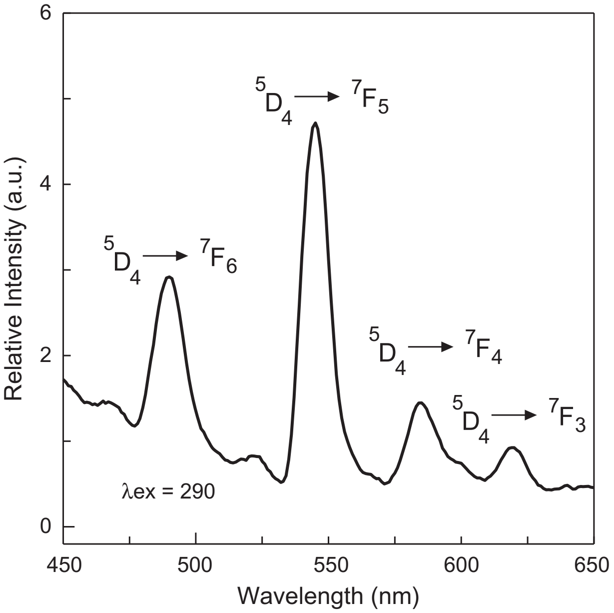


Figure 5. Emission spectrum of [Tb(Pyrrol-Dtc)$_3$(Phen)].

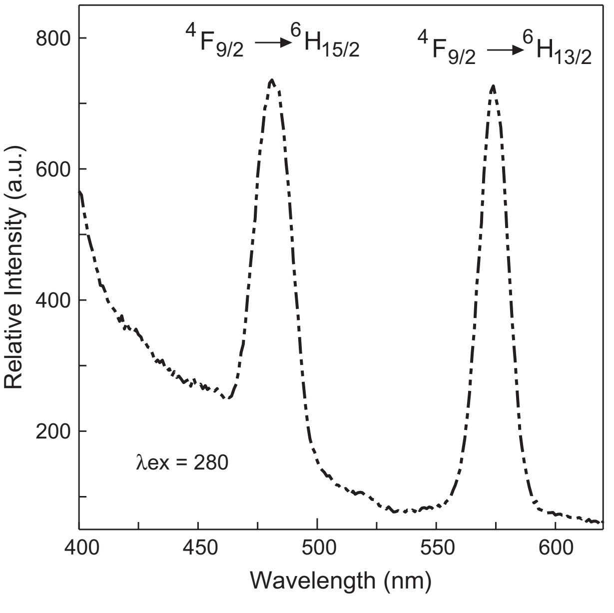
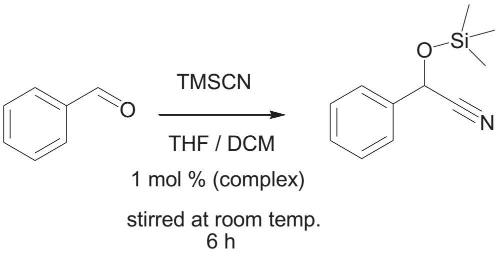


Figure 6. Emission spectrum of [Dy(Pyrrol-Dtc)$_3$(Phen)].



Scheme 2. Catalytic activity.

Table 4. Percentage yields of the product obtained in trimethylsilylcyanation reaction.

| Compound | DCM, yield (%) | THF, yield (%) |
|---|---|---|
| [La(Pyrrol-Dtc)$_3$(Phen)] | 72 | 90 |
| [Ce(Pyrrol-Dtc)$_3$(Phen)] | 80 | 95 |
| [Pr(Pyrrol-Dtc)$_3$(Phen)] | 90 | 98 |
| [Nd(Pyrrol-Dtc)$_3$(Phen)] | 85 | 95 |
| [Sm(Pyrrol-Dtc)$_3$(Phen)] | 76 | 89 |
| [Gd(Pyrrol-Dtc)$_3$(Phen)] | 75 | 96 |
| [Tb(Pyrrol-Dtc)$_3$(Phen)] | 78 | 92 |
| [Dy(Pyrrol-Dtc)$_3$(Phen)] | 65 | 85 |
| [Er(Pyrrol-Dtc)$_3$(Phen)] | 85 | 97 |

The consumption of benzaldehyde was monitored by TLC. Yields refer to the isolated product.

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 using 3–5% of ethyl acetate in petroleum ether to give pure product as a colorless liquid. The product was characterized using $^1$H NMR spectrum (figure S10). The overall reaction is shown in scheme 2, and the percentage yields obtained are collected in table 4.

The results given in table 4 indicated that the reaction carried out in THF gave excellent yields when compared to that in DCM. The results also indicated that the good to excellent yields obtained were with just 1 mol% catalyst in 6 h at RT and are comparable with those reported using 10 mol% transition metal and lanthanide complexes as catalyst [28, 29]. The advantages of the present Ln(III) complexes over those reported are the most simple preparation method with good yields, anhydrous nature of the complexes, and solubility of the complexes in common organic solvents.

## 4. Conclusion

A series of nine lanthanide(III) pyrrolidine dithiocarbamate complexes have been synthesized and structurally characterized. The molecular structures of [La(Pyrrol-Dtc)$_3$(Phen)], [Pr(Pyrrol-Dtc)$_3$(Phen)], [Sm(Pyrrol-Dtc)$_3$(Phen)], and [Dy(Pyrrol-Dtc)$_3$(Phen)] were confirmed by single crystal XRD studies which revealed that in these complexes, the central

Ln(III) ion possesses a distorted dodecahedral geometry. The use of these complexes as catalyst in trimethylsilylcyanation gave good to excellent yields of the product with 1 mol% catalyst at RT in 6 h.

## Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center with CCDC numbers for [La(Pyrrol-Dtc)$_3$(Phen)], 829383; [Pr(Pyrrol-Dtc)$_3$(Phen)], 888071; [Sm(Pyrrol-Dtc)$_3$(Phen)], 962697; and [Dy(Pyrrol-Dtc)$_3$(Phen)] 871334, 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 Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223 336 033; or Email: deposit@ccdc.cam.ac.uk.

## Disclosure statement

No potential conflict of interest was reported by the authors.

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