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#### Synthesis, spectral characterization, crystal structures and catalytic activity

### of a series of lanthanide(III) azepane dithiocarbamate complexes<sup>‡</sup>

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#### ABSTRACT

A series of lanthanide(III) azepane dithiocarbamate (Aze-Dtc) complexes, [Ln(Aze-Dtc)<sub>3</sub>(Phen)] where Ln = La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III) and Er(III), have been synthesized under mild reaction conditions with excellent yields. The new complexes have been structurally characterized by analytical (CHNS) and various spectral techniques, such as FT-IR, UV–Vis, CV and <sup>1</sup>H NMR. The coordination mode of the ligands and the geometry of [Pr(Aze-Dtc)<sub>3</sub>(Phen)], [Nd(Aze-Dtc)<sub>3</sub>(Phen)], [Sm(Aze-Dtc)<sub>3</sub>(Phen)] and [Dy(Aze-Dtc)<sub>3</sub>(Phen)] were confirmed by single crystal X-ray studies. In these complexes the central Ln(III) atom possess a distorted dodecahedral geometry with six sulfur atoms of three Aze-Dtc ligands and two nitrogen atoms of a 1,10-phenanthroline ligand coordinated to it. The utility of these complexes as catalysts in trimethylsilylcyanation of carbonyl compounds has also been screened. The results indicate that the catalytic activity shown by these complexes is good to excellent.

Keywords: Lanthanide, dithiocarbamate, 1,10-phenanthroline, silylcyanation

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#### **1. Introduction**

Over the years, the synthesis of lanthanide complexes with a variety of ligands has received considerable interest because of their potential applications in various fields [1-10]. Hence, the synthesis and characterization of newer lanthanide complexes is an ever green field of research in inorganic chemistry. Though Jorgensen et al. [11] reported the first lanthanide-dithiocarbamate complexes during the 1960s, a literature review indicated that the study of such complexes is relatively less when compared to that their transition metal analogues. Recently, there has been a renaissance of interest in these complexes for a variety of uses [12,13] and hence the present study.

Cyanohydrins are well-known natural products and versatile synthetic intermediates for pharmaceuticals and agrochemicals, and they are also excellent starting materials for the preparation of several important classes of organic compounds [14]. A review of the literature revealed that transition metal complexes have been widely used as catalysts in trimethylsilylcyanation of carbonyl compounds [15-18]. However, the use of lanthanide complexes in such reactions is relatively less studied in the literature [19,20].

The main objective, therefore, of this endeavor is to synthesize a series of Ln(III) complexes of azepane dithiocarbamate (Aze-Dtc), as such ligands possess a wide variety of applications. The complexes were characterized using several analytical and spectral techniques and crystal structures of four of the complexes were determined. The usefulness of these complexes as a catalyst in trimethylsilylcyanation of carbonyl compounds is also demonstrated.

#### 2. Experimental

#### 2.1 Materials and methods

All the chemicals were of commercially available high purity grade (Aldrich) and were used as received. The ligand Aze-Dtc has been synthesized according to the literature

procedure, with a slight modification [21]. Elemental analyses (CHNS) were carried out on an Elementar Vario EL III at the Sophisticated Test and Instrumentation Centre 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 in the range 4000–400 cm<sup>-1</sup>. Electronic spectra of the complexes were recorded on a JASCO, Japan (V-630) double beam spectrophotometer. <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>). HPLC studies were carried out on Shimadzu CLASS-VP Ver. 6.14 SP2 instrument. 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 glassy carbon working electrode, a platinum wire as a reference electrode and a platinum wire as an 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 Ka 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 (Aze-Dtc)

The ligand was prepared by adopting the following procedure [21]. Sodium hydroxide (0.05 mol) was dissolved in 3 mL of water in an ice bath and 50 mL of ethanol was added to it. The solution was stirred vigorously, during which time azepane (0.05 mol) was added, then carbon disulfide (0.05 mol) was added slowly drop by drop which yielded the

precipitation of the dithiocarbamate sodium salt. The mixture was stirred for a further 30 minutes for the reaction to complete. The yellow product was collected by filtration, redissolved in a minimum amount of methanol and the pure white product was precipitated by adding the required volume of diethyl ether. Anal. Calc. for  $C_7H_{12}NS_2Na$ : C, 42.61; H, 6.13; N, 7.10; S, 32.50%. Found: C, 42.50; H, 6.20; N, 7.22; S, 32.60%. FT-IR (KBr, cm<sup>-1</sup>): 3378s, 3178m, 2978m, 2934s, 2851s, 2102b, 1623s, 1483s, 1448s, 1409s, 1365s, 1258s, 1187s, 1095m, 1047s, 975s, 953s, 904m, 850s, 762m, 538m, 454m. <sup>1</sup>H NMR (Fig. S1) (DMSO-d<sub>6</sub>,  $\delta$  ppm): 1.43 (t, *J* = 3Hz, 4H), 1.67 (m, 4H), 4.14 (t, *J* = 6Hz, 4H). UV-Vis (Chloroform, cm<sup>-1</sup>) (log  $\epsilon$ ): 38500 (3.92), 35300 (3.95). Yield 85%.

#### 2.3 Preparation of the lanthanum(III) complexes

The [Ln(Aze-Dtc)<sub>3</sub>(Phen)] complexes {where Ln=La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III) and Er(III)} (1-9) were prepared by mixing methanolic solutions of LnCl<sub>3</sub>.6H<sub>2</sub>O (0.5 mmol) and a mixture of Aze-Dtc (1.5 mmol) and Phen (0.5 mmol). In each case, on stirring the mixture at room temperature the complex precipitated as a fine powder. The complex was filtered and washed with methanol, which yielded the pure product. The complexes are freely soluble in chloroform, dichloromethane, DMF and DMSO. The analytical and spectral data of the complexes are given below.

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

Anal. Calc. for C<sub>33</sub>H<sub>44</sub>LaN<sub>5</sub>S<sub>6</sub>: C, 47.07; H, 5.27; N, 8.32; S, 22.85%. Found: C, 46.93; H, 5.00; N, 8.32; S, 22.60%. FT-IR (KBr, cm<sup>-1</sup>): 2922s, 2851m, 2361m, 1482s, 1450, 1416s, 1362s, 1264s, 1187s, 1096m, 848s, 723s, 453m. <sup>1</sup>H NMR (Fig. S2) (DMSO-d<sub>6</sub>,  $\delta$  ppm): 1.43 (s, 12H), 1.68 (s, 12H), 4.06-4.11 (m, 12H), 7.81 (s, 2H), 8.02 (s, 2H), 8.52 (d, *J* = 9Hz, 2H), 9.16 (s, 2H). UV-Vis (Chloroform, cm<sup>-1</sup>) (log  $\varepsilon$ ): 43900 (4.00), 37300 (4.15). Yield 80%.

2.3.2  $[Ce(Aze-Dtc)_3(Phen)]$  (2)

Anal. Calc. for  $C_{33}H_{44}CeN_5S_6$ : C, 47.07; H, 5.26; N, 8.31; S, 22.82%. Found: C, 47.12; H, 5.24; N, 8.31; S, 22.80%. FT-IR (KBr, cm<sup>-1</sup>): 2922s, 2851m, 2360m, 1573s,1482s, 1447s, 1411s, 1366s, 1287m, 1262s, 1096m, 1047m, 981s, 888m, 844s, 726s, 621w, 436m. UV-Vis (Chloroform, cm<sup>-1</sup>) (log  $\varepsilon$ ): 44100 (3.91), 37700 (3.84). Yield 92%.

#### 2.3.3 $[Pr(Aze-Dtc)_3(Phen)]$ (3)

Anal. Calc. for  $C_{33}H_{44}PrN_5S_6$ : C, 46.96; H, 5.25; N, 8.30; S, 22.79%. Found: C, 46.96; H, 5.24; N, 8.28; S, 22.80%. FT-IR (KBr, cm<sup>-1</sup>): 2920s, 2850m, 2361m, 1481s, 1449, 1262s, 1186s, 1094m, 980m, 848s, 766s, 627s, 453m. <sup>1</sup>H NMR (Fig. S3) (DMSO-d<sub>6</sub>,  $\delta$  ppm): 0.34 (s, b, 24H), 2.25 (s, 12H), 7.47 (s, b, 2H), 7.74 (s, b 2H), 8.22 (s, b, 2H), 8.78 (s, b, 2H). UV-Vis (Chloroform, cm<sup>-1</sup>) (log  $\epsilon$ ): 43900 (4.04), 37200 (4.15). Yield 99%.

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

Anal. Calc. for C<sub>33</sub>H<sub>44</sub>NdN<sub>5</sub>S<sub>6</sub>: C, 46.77; H, 5.23; N, 8.26; S, 22.70%. Found: C, 46.70; H, 5.24; N, 8.28; S, 22.68%. FT-IR (KBr, cm<sup>-1</sup>): 2922s, 2851m, 2361m, 2336m 1482s, 1411, 1264s, 1186s, 1097m, 982m, 852s, 775s, 723s, 628s, 451m. <sup>1</sup>H NMR (Fig. S4) (DMSO-d<sub>6</sub>,  $\delta$  ppm): 1.05-1.19 (m, 12H), 1.43 (s, 12H), 3.84 (s, 12H), 7.79 (s, 2H), 8.01 (s, 2H), 8.51 (d, *J* = 9Hz, 2H), 9.11 (s, 2H). UV-Vis (Chloroform, cm<sup>-1</sup>) (log  $\varepsilon$ ): 43900 (4.10), 37200 (4.23). Yield 95%.

#### 2.3.5 [Sm(Aze-Dtc)<sub>3</sub>(Phen)] (5)

Anal. Calc. for  $C_{33}H_{44}SmN_5S_6$ : C, 46.44; H, 5.20; N, 8.21; S, 22.54%. Found: C, 46.23; H, 5.20; N, 8.20; S, 22.58%. FT-IR (KBr, cm<sup>-1</sup>): 2922s, 2851m, 2361m, 1484s, 1412s, 1264s, 1186s, 1096m, 982m, 852s, 775s, 630s, 464m. <sup>1</sup>H NMR (Fig. S5) (DMSO-d<sub>6</sub>,  $\delta$  ppm): 1.38 (d, J = 3Hz, 12H), 1.63 (s, 12H), 3.95 (s, 12H), 7.86-7.80 (m, 2H), 8.01 (s, 2H), 8.52 (d, J = 3Hz, 2H), 9.11 (d, J = 3Hz, 2H). UV-Vis (Chloroform, cm<sup>-1</sup>) (log  $\varepsilon$ ): 43900 (4.05), 37300 (4.15). Yield 98%.

2.3.6  $[Gd(Aze-Dtc)_3(Phen)]$  (6)

Anal. Calc. for  $C_{33}H_{44}GdN_5S_6$ : C, 46.07; H, 5.15; N, 8.14; S, 22.36%. Found: C, 46.00; H, 5.20; N, 8.16; S, 21.96%. FT-IR (KBr, cm<sup>-1</sup>): 2925s, 2852m, 2360m, 1491s, 1441, 1267s, 1191s, 1098m, 983m, 849s, 760s, 632s, 464m. UV-Vis (Chloroform, cm<sup>-1</sup>) (log  $\varepsilon$ ): 43900 (3.78), 37200 (3.90). Yield 84%.

2.3.7  $[Tb(Aze-Dtc)_3(Phen)]$  (7)

Anal. Calc. for C<sub>33</sub>H<sub>44</sub>TbN<sub>5</sub>S<sub>6</sub>: C, 45.98; H, 5.14; N, 8.12; S, 22.32%. Found: C, 45.90; H, 5.00; N, 7.98; S, 22.45%. FT-IR (KBr, cm<sup>-1</sup>): 2921s, 2851m, 2361m, 1483s, 1412, 1264s, 1186s, 1095m, 984m, 852s, 776s, 628s, 459m. UV-Vis (Chloroform, cm<sup>-1</sup>) (log ε): 44100 (3.78), 37000 (3.80). Yield 85%.

2.3.8 [Dy(Aze-Dtc)<sub>3</sub>(Phen)] (8)

Anal. Calc. for  $C_{33}H_{44}DyN_5S_6$ : C, 45.63; H, 5.45; N, 8.06; S, 22.15%. Found: C, 45.96; H, 5.20; N, 8.08; S, 22.20%. FT-IR (KBr, cm<sup>-1</sup>): 2924s, 2851m, 2360m, 1479s, 1441, 1266s, 1190s, 1098m, 983m, 849s, 781s, 632s, 455w. UV-Vis (Chloroform, cm<sup>-1</sup>) (log  $\varepsilon$ ): 43900 (4.08), 37300 (4.25). Yield 86%.

2.3.9 [Er(Aze-Dtc)<sub>3</sub>(Phen)] (9)

Anal. Calc. for  $C_{33}H_{44}ErN_5S_6$ : C, 45.38; H, 5.42; N, 8.02; S, 22.03%. Found: C, 45.82; H, 5.20; N, 8.20; S, 22.50%. FT-IR (KBr, cm<sup>-1</sup>): 2924s, 2852m, 2360m, 1478s, 1441s, 1267s, 1191s, 1098m, 984m, 850s, 781s, 633s, 455w. UV-Vis (Chloroform, cm<sup>-1</sup>) (log  $\varepsilon$ ): 44100 (3.97), 37200 (4.08). Yield 99%.

2.4 X-ray crystallography

The single crystals of **3**, **4**, **5** and **8** were prepared by the solvent diffusion method using chloroform and diethyl ether as the solvents. X-ray single-crystal diffraction data for these complexes were collected and the crystallographic data and experimental details for the structural analyses are summarized in Table 1. The most important bond lengths between the metal and coordinating ligand atoms and their bond angles are listed in Table 2.

#### 3. Results and discussion

The nine [Ln(Aze-Dtc)<sub>3</sub>(Phen)] complexes 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(Aze-Dtc)<sub>3</sub>(Phen)], [Nd(Aze-Dtc)<sub>3</sub>(Phen)], [Sm(Aze-Dtc)<sub>3</sub>(Phen)] and [Dy(Aze-Dtc)<sub>3</sub>(Phen)] were determined and discussed. The catalytic activity of these complexes in the trimethylsilylcyanation of carbonyl compounds was also screened.

#### 3.1 Crystal structures

The crystal structure of complexes **3**, **4**, **5** and **8** are shown in Figures 1 to 4, respectively, and the crystallographic data are given in Table 1. Selected bond angles and bond lengths are collected in Table 2. It is evident from these figures that the geometry of the crystals is distorted dodecahedral around the eight coordinated metal ion. The distortion in the coordination sphere of the metal ion from the ideal geometry may be due to the structural constraints imposed by the bulky Phen ligand framework. There are three dithiocarbamate ligands coordinated through six sulfur atoms, and the Phen ligand is coordinated through two nitrogen atoms.

The obtained results of the bond angles (°) of the three dithiocarbamate ligands in these crystals are interesting (Table 2). The S-Ln-S bond angles for the two dithiocarbamate ligands which are in an 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 are higher than that of the axial ligand.

The following general conclusions were drawn from the foregoing results. All the four compounds investigated crystallized in a triclinic system with the space group P-1. All the four lanthanide crystals investigated are comparable with their analogues reported in the

literature [22-24]. In these four compounds, the average length (Å) of the C-S bond is 1.720 Å, which is significantly shorter than the C–S single bond length (1.81 Å) and higher than the C=S distance (1.69 Å). The observed intermediate value between the C–S and C=S bond distance indicates partial double bond character in these complexes [25].

#### 3.2 FT-IR study

Since, the FT-IR spectra of all the complexes are similar, the important details of the FT-IR spectrum of  $[Pr(Aze-Dtc)_3(Phen)]$  is 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 a water molecule. The FT-IR spectrum of the free dithiocarbamate ligand exhibits a doublet at 975 and 953 cm<sup>-1</sup>, corresponding to the vC-S stretching [26]. In the complex, it appears as a singlet at 982 cm<sup>-1</sup>, indicating coordination of the ligand in a bidentate manner with the metal ion [27]. The peak corresponding to the vC-N stretching in the free Phen ligand appeared at 1455 cm<sup>-1</sup>, and this peak experienced a shift to 1481 cm<sup>-1</sup> in the complex, suggesting the coordination of Phen with Pr(III) through the two nitrogen atoms.

#### 3.3 <sup>1</sup>H NMR study

The proton NMR spectra of Aze-Dtc and complexes **1**, **3**, **4** and **5** were recorded in DMSO-d<sub>6</sub> solvent and are given in figures S1-S5 (Supplementary data). The spectral data are collected in the experimental section. In the Aze-Dtc ligand three peaks appeared at 1.43, 1.67 and 4.14 ppm, corresponding to the twelve aliphatic protons. In the complexes, the observed broadening of the peaks may be due to significant electron delocalization between the metal and the ligands [28].

#### **3.4 Electronic absorption study**

Electronic absorption spectra of the ligands (Aze-Dtc and Phen), complexes **3-5** and the corresponding hydrated metal salts were recorded (Fig. S6-S8), and representative spectra

are given in Figure 5. It is evident from Figure S6 that there are two intense peaks appearing in the UV region, i.e. at 44052 and 37735 cm<sup>-1</sup>, for the Phen ligand and two medium intensity peaks at 38461 and 35335 cm<sup>-1</sup> for the Aze-Dtc ligand. In the complexes they appear around 43859 and 37313 cm<sup>1</sup>, respectively. The first band, at the longer wave number, was assigned to the  $\pi \rightarrow \pi^*$  transition of the aromatic ligand and the second very intense band is the result of the overlapping of absorption peaks of the Phen and the Aze-Dtc ligands [22,29].

In the electronic spectra of the complexes, a number of very weak and narrow peaks (Fig. 5), which are characteristic of the Laporte forbidden f-f transitions of the Ln(III) ions, are observed in the visible region [30]. In the present case, the assignments of the peaks were made by a comparison with the spectra of the Ln(III) aquo ions in dilute acid solution [31,32]. As representative cases, the f-f transitions observed for complexes **3-5** are collected in Table 3. In the spectrum of the Pr(III) complex (Fig. 5), it is interesting to note that a small peak that corresponds to the  ${}^{3}\text{H}_{4} \rightarrow {}^{1}\text{I}_{6}$  transition is observable, which is absent in the spectrum of the Pr(III) aquo ion. This transition is hypersensitive to the environment about the Pr(III) ion [22,33-35].

A perusal of the results in Table 3 indicate that the electronic spectra of the Ln(III) complexes show a general red shift of all the f-f spectral bands in comparison with those of their corresponding aquo ions [36]. 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 the occurrence of some covalent character in the metal-ligand bond [35,37]. 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 ions [38]. The absorption bands in the visible region for

Pr(III), Nd(III) and Sm(III) are due to the transition from the ground levels  ${}^{3}H_{4}$ ,  ${}^{4}I_{9/2}$  and  ${}^{6}H_{5/2}$  respectively to the excited J level of the 4f configuration [39].

#### **3.5 Electrochemical properties**

The solution electrochemical behavior of the ligands and a representative complex, [Pr(Aze-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 was investigated. The cyclic voltammogram recorded at a scan rate of 20 mV s<sup>-1</sup>, using a three electrode system, is shown in Figure 6. Glassy carbon (GC) was used as the working electrode and Pt wire as reference and auxiliary electrodes. The GC electrode was polished with an alumina slurry before each run. The cyclic voltammogram of the Phen ligand exhibited three oxidation peaks, at -0.327, 0.332 and 1.109 V, and a reduction peak at -0.942 V. The Aze-Dtc ligand also exhibited three oxidation peaks, at 0.464, 0.730 and 0.930V, and a reduction peak at -0.98 V. The complex exhibited two oxidation peaks (0.220 and 1.088 V) and a reduction peak (-1.095 V). Since the oxidation state of the central trivalent lanthanide ion does not change, the electrochemical behavior observed in the complex is due to successive removal or addition of electrons from or to the ligand-based orbitals [40]. The observed results indicate that the oxidation potential of the Aze-Dtc ligand shows a significant shift in the complex, as compared to the free ligand. The oxidation potential in the complex is more positive than that in the free ligand, which suggests that the oxidation of the Aze-Dtc ligand in the complex is relatively difficult. This may be due to the fact that the ligand gives electrons on forming coordinate bonds which makes the oxidation difficult.

#### **3.6 Catalytic activity**

The usefulness of these complexes as a catalyst in trimethylsilylcyanation of carbonyl compounds has been investigated in dicholoromethane and tetrahydrofuran solvents. In a typical experiment, to a stirred solution of 1 mol % [Ln(Aze-Dtc)<sub>3</sub>(Phen)] in a given solvent, 0.5 mL of benzaldehyde was added at room temperature under a nitrogen atmosphere. Then 1.1 mL of trimethylsilyl cyanide was added to the reaction mixture, followed by stirring for 6

h under an 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% ethyl acetate in pet-ether to give the pure product as a colorless liquid. The product was characterized using its <sup>1</sup>H NMR spectrum (Fig. S9). The overall reaction is shown in Scheme 2 and the percentage yields obtained are collected in Table 4.

Brunel and Holmes [41] have reviewed the development of chemically catalyzed asymmetric cyanohydrin syntheses. Many metal [Ti(IV), V(IV), Sn(II), Mg(II), Al(III), etc. ] and a 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. [20] have reported the use of lanthanide-dithiocarbamate complexes as catalysts in such a reaction, giving 65-98% yields of the product. However, the time required was reported to be 6-11 h. In the present study, the results indicate that the good to excellent yields obtained, with 1 mol% catalyst in 6 h at RT, are comparable with those reported using transition metal and lanthanide complexes as catalysts [15-20]. 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.

#### Appendix A. Supplementary data

CCDC numbers 845968, 871332, 871336 and 845969 contains the supplementary crystallographic data for the complexes [Pr(Aze-Dtc)<sub>3</sub>(Phen)] (**3**), [Nd(Aze-Dtc)<sub>3</sub>(Phen)] (**4**), [Sm(Aze-Dtc)<sub>3</sub>(Phen)] (**5**) and [Dy(Aze-Dtc)<sub>3</sub>(Phen)] (**8**) given as CIF files. Figures S1-S9 contains the supplementary data for this paper. Crystallographic 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.

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#### **Figure captions**

- **Figure 1:** Molecular structure of [Pr(Aze-Dtc)<sub>3</sub>(Phen)] · CHCl<sub>3</sub>
- Figure 2: Molecular structure of [Nd(Aze-Dtc)<sub>3</sub>(Phen)] · CHCl<sub>3</sub>
- Figure 3: Molecular structure of [Sm(Aze-Dtc)<sub>3</sub>(Phen)] · CHCl<sub>3</sub>
- Figure 4: Molecular structure of [Dy(Aze-Dtc)<sub>3</sub>(Phen)] · CHCl<sub>3</sub>
- **Figure 5**. Electronic f-f transitions in the visible region of  $PrCl_3.6H_2O$  (red) and [Pr(Aze-Dtc)<sub>3</sub>(Phen)] (blue)
- Figure 6. Cyclic voltammagram of a) Phen (red) b) [Pr(Aze-Dtc)<sub>3</sub>(Phen)] (green)
  c) Aze-Dtc (blue) in 0.1M [Bu<sub>4</sub>N][ClO<sub>4</sub>]/CH<sub>2</sub>Cl<sub>2</sub> at a scan rate of 20 mV s<sup>-1</sup>
- Scheme 1. Preparation of the [Ln(Aze-Dtc)<sub>3</sub>(Phen)] complexes
- Scheme 2. Catalytic activity

## Figure 1.



# Figure 3.



### Figure 5.



### Scheme 1.



Complex	3	4	5	8
Empirical Formula	$C_{34}H_{45}Cl_3N_5S_6Pr$	$C_{34}H_{45}Cl_3N_5S_6Nd$	$C_{34}H_{45}Cl_3N_5S_6Sm$	$C_{34}H_{45}Cl_3N_5S_6Dy$
Formula Weight	963.37	966.70	972.81	985.00
Crystals system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1	P-1
a (Å)	10.719(3)	10.5907(10)	10.5911(10)	10.6929(9)
b (Å)	13.007(4)	12.9441(2)	12.9490(10)	12.8900(11)
c (Å)	16.970(5)	16.6542(2)	16.6522(2)	16.8326(15)
α(°)	67.747(6)	67.6950(10)	67.70	67.988(2)
β(°)	80.692(6)	86.5540(10)	86.5630(10)	80.353(2)
γ(°)	72.524(6)	72.8810(10)	72.92	72.987(2)
Volume (Å <sup>3</sup> )	2085.6(11)	2015.22(4)	2016.33(3)	2052.4(3)
Z	2	2	2	2
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Density	1.534	1.593	1.602	1.555
(calc) (Mg/m <sup>3</sup> )				
Abs Coefficient	1.692	1.830	1.998	2.351
(mm <sup>-1</sup> )	0			
Crystal size (mm <sup>3</sup> )	0.12x0.10x0.08	0.24x0.15x0.10	0.14x0.10x0.08	0.10x0.08x0.06
θ range (°)	0.998-25.00	1.32-26.50	2.89-28.44	1.31-25.00
Reflections	7339	8293	8301	7181
Collected				
Independent	6505	7722	7913	6173
Reflections				
Data / Restraints /	6505/0/442	7722/0/422	7913/0/442	6173/0/442
Parameters				
F(000)	980	982	986	946
R1/wR2	0.0327/0.0820	0.0217/0.0629	0.0208/0.0557	0.0345/0.0766

 Table 1. Summary of the crystallographic data for the complexes 3-5 and 8

	3		4	5		8	
Bond lengths (	Å)						
Pr1-S2	2.9121(12)	Nd1-S1	2.8876(7)	Sm1-S1	2.8935(6)	Dy1-S26	2.8415(12)
Pr1-S4	2.8522(13)	Nd1-S2	2.8381(7)	Sm1-S2	2.8879(6)	Dy1-S18	2.8381(12)
Pr1-S12	2.9062(12)	Nd1-S3	2.8939(7)	Sm1-S3	2.9034(6)	Dy1-S38	2.8228(12)
Pr1-S14	2.9030(13)	Nd1-S4	2.8882(7)	Sm1-S4	2.8745(6)	Dy1-S36	2.8164(13)
Pr1-S22	2.9204(13)	Nd1-S5	2.9026(7)	Sm1-S5	2.8392(6)	Dy1-S35	2.7594(12)
Pr1-S24	2.8858(12)	Nd1-S6	2.8745(7)	Sm1-S6	2.8863(6)	Dy1-S16	2.7901(12)
Pr1-N32	2.649(3)	Nd1-N4	2.651(2)	Sm1-N4	2.6512(19)	Dy1-N13	2.594(3)
Pr1-N43	2.681(3)	Nd1-N5	2.626(2)	Sm1-N5	2.6299(19)	Dy1-N2	2.545(3)
Bond angles (°	')						
S2-Pr1-S4	61.68(3)	S1-Nd1-S2	62.250(19)	S1-Sm1-S2	61.657(16)	S16-Dv1-S18	63.27(3)
S12-Pr1-S14	61.03(3)	S3-Nd1-S4	61.648(19)	S3-Sm1-S4	61.963(16)	S26-Dv1-S35	63.40(3)
S22-Pr1-S24	61.40(4)	S5-Nd1-S6	61.965(19)	S5-Sm1-S6	62.251(16)	S36-Dy1-S38	62.65(4)
N32-Pr1-N43	62.21(9)	N4-Nd1-N5	63.04(7)	N4-Sm1-N5	63.15(6)	N2-Dy1-N13	64.68(11)
Averages	0						
Bond lengths (.	Á)						
Pr-S	2.8966(12)	Nd-S	2.8808(7)	Sm-S	2.8808(6)	Dy-S	2.8114(12)
Pr-N	2.665(3)	Nd-N	2.6385(2)	Sm-N	2.6405(19)	Dy-N	2.5695(3)
C-S	1.7208(4)	C-S	1.7267(3)	C-S	1.7265(2)	C-S	1.720(4)
Bond angles ( $^{o}$	)						
S-Pr-S	61.37(3)	S-Nd-S	61.9543(19)	S-Sm-S	61.957(16)	S-Dy-S	63.1067(3)
S-C-S	118.3667(14)	S-C-S	118.373(14)	S-C-S	118.37(15)	S-C-S	117.6333(3)
			8				

 Table 2. Selected bond parameters of complexes 3, 4, 5 and 8

Complexes	Ln(III) aqua ion (cm <sup>-1</sup> )	Complex (cm <sup>-1</sup> )	log ε	Red shift (cm <sup>-1</sup> )	Covalent parameter
$[Pr(Aze_Dtc)_(Phen)]$	22500	21900	2 67	100	R = 0.071
	-	21100	2.52	-	p = 0.971 $\delta\% = 2.99$
	21400	20800	2.53	400	$b^{1/2} = 0.121$
	20800	20100	2.48	700	
	17000	16500	2.32	500	
[Nd(Aze-Dtc) <sub>3</sub> (Phen)]	21600	21000	2.20	600	$\beta = 0.967$
	20000	19200	2.16	800	<i>8</i> % = 3.46
	19900	18800	2.18	1100	$b^{1/2} = 0.127$
	17900	16900	2.31	1000	
	16200	15900	2.91	300	
	14900	14600	1.85	300	
	13700	13300	2.25	400	
	12700	12300	2.34	400	
[Sm(Aze-Dtc) <sub>2</sub> (Phen)]	05000	24000	2.26	1000	8-0.981
	25000	24000	1.00	1000	p = 0.704
	24100	23400	1.90	700	0% = 1.68
	21600	21400	1.43	200	$b^{1/2} = 0.095$
	20900	20800	1.36	100	

### Table 3. Electronic absorption spectral data and related bonding parameters

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Compound	DCM	THF
Compound	Yield %	Yield %
[La(Aze-Dtc) <sub>3</sub> (Phen)]	85	80
[Ce(Aze-Dtc) <sub>3</sub> (Phen)]	77	68
[Pr(Aze-Dtc) <sub>3</sub> (Phen)]	63	92
[Nd(Aze-Dtc) <sub>3</sub> (Phen)]	81	86
[Sm(Aze-Dtc) <sub>3</sub> (Phen)]	66	50
[Gd(Aze-Dtc) <sub>3</sub> (Phen)]	52	58
[Tb(Aze-Dtc) <sub>3</sub> (Phen)]	75	73
[Dy(Aze-Dtc) <sub>3</sub> (Phen)]	67	85
[Er(Aze-Dtc) <sub>3</sub> (Phen)]	90	95

**Table 4.** Percentage yields of the products obtained in the trimethylsilylcyanation

 reaction

The consumption of benzaldehyde was observed by TLC.

Yields refer to the isolated products.

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# Synthesis, spectral characterization, crystal structures and catalytic activity of a series of lanthanide(III) azepane dithiocarbamate complexes

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# Synthesis, spectral characterization, crystal structures and catalytic activity of a series of lanthanide(III) azepane dithiocarbamate complexes

Ponnuchamy Pitchaimani, Kong Mun Lo and Kuppanagounder P.Elango\*

A series of lanthanide(III) azepane dithiocarbamate complexes have been synthesized and characterized by single crystal X-ray studies, and their catalytic activities in the trimethylsilylcyanation of carbonyl compounds has been screened.