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THERMAL STUDIES ON SOME LANTHANIDE(III) COMPLEXES OF HEXAMETHYLENEDITHIOCARBAMATE

KRISHAN KUMAR DAHIYA and NARENDER KUMAR KAUSHIK *
Department of Chemistry, University of Delhi, Delhi-110007 (India)

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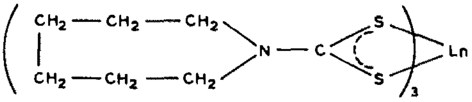
ABSTRACT

Hexamethylenedithiocarbamate complexes of lanthanides of the type $Ln(C_6H_{12}NCS_2)_3$ (where Ln ≡ La, Pr, Nd, Sm, Tb and Dy) were synthesized. Spectral studies (IR and UV) indicate that the hexamethylenedithiocarbamate moiety is bidentate. Thermogravimetric studies reveal that the complexes undergo volatilization without decomposing. The heats of vaporization were calculated from the differential thermal analysis curves.

INTRODUCTION

The chemistry of dithiocarbamate complexes of transition metals continues to be of great interest because of their striking structural features and diversified applications [1,2]. The compounds derived from dithiocarbamate ligands have been used in industry as vulcanization accelerators and as high pressure lubricants. Their use as fungicides and pesticides has induced a vast number of biological and biochemical studies [3]. In this paper we report the results of TG and DTA studies of some lanthanide(III) hexamethylenedithiocarbamate complexes. In agreement with earlier investigations on thermal studies of metal dithiocarbamates [4,5], these complexes are volatile at elevated temperatures.



(I)

Ln = La, Pr, Nd, Sm, Tb, Dy

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* Author for correspondence.

EXPERIMENTAL

The following instruments were used: a Shimadzu IR spectrophotometer (IR-435) for the measurement of IR spectra; a Perkin–Elmer UV–visible spectrophotometer (model 554) for the measurement of UV spectra; a Stanton Redcroft STA-780 for the recording of the TG and DTA curves up to 1273 K in air (heating rate, $10\,^\circ C\ min^{-1}$; chart speed, $50\ cm\ h^{-1}$).

Sodium hexamethylenedithiocarbamate was prepared by the modified method given by Gilman and Blatt [6]. Anhydrous trichlorides (MCl_3) of the lanthanides were prepared by the method reported by Taylor and Carter [7]. The trivalent lanthanide dithiocarbamates of the type $M(C_6H_{12}NCS_2)_3$ (where $M \equiv$ La, Pr, Nd, Sm, Tb and Dy) were prepared in a dry inert atmosphere using ethanolic solutions of the metal trichloride and the ligand in the stoichiometric ratio 1 : 3. A weighed quantity of the ligand, sodium hexamethylenedithiocarbamate, was dissolved in absolute ethanol (~ 20 ml). Dry nitrogen gas was then passed through the solution for about 15 min. Absolute ethanol (~ 25 ml) was placed in another flask and dry nitrogen gas was passed through it for about 15 min. A weighed quantity of anhydrous metal chloride was dissolved in it carefully and then the solution was flushed once again with dry nitrogen gas for ~ 20 min to remove any oxygen. The metal chloride solution was mixed with the ligand solution through a transfer tube with shaking. The reaction mixture was refluxed for 30–45 min during which time it was protected from moisture by guard tubes filled with fused calcium chloride. The solvent was removed under reduced pressure and the residue was extracted into acetonitrile (~ 45 ml). The solution was filtered through a specially designed sintered glass disc provided with standard joints at both ends and an outlet tube for suction in the lower limb. The filtrate was collected with great care and was concentrated under reduced pressure to about one-third of its original volume. Anhydrous petroleum ether (60–80 °C) (~ 30 ml) was added to it with vigorous shaking. Solid crystals separated out. These were filtered, washed with ether and dried in vacuo. They were then recrystallized from acetonitrile.

RESULTS AND DISCUSSION

The mode of bonding of hexamethylenedithiocarbamate ligand with the lanthanide(III) ions was ascertained using IR and UV spectral studies. Whether the dithiocarbamate group is monodentate or bidentate is reflected in the $\nu(C \overset{\ldots}{-} S)$ stretching frequency. The presence of only one strong band in the $\sim 1000\ cm^{-1}$ region supports a bidentate behaviour of the dithiocarbamates, whereas a doublet is expected in the $1000 \pm 50\ cm^{-1}$ region for monodentate behaviour [8–10]. The complexes studied in this work possess only one absorption band in the $1000\ cm^{-1}$ region, which supports the bidentate behaviour of the dithiocarbamate ligand, and also suggests that the ligand is chelated in all the complexes. The free ligand shows a doublet at 980 and 1005 cm^{-1}.

In the UV region an intense band appears at ca. 260 nm (log $\epsilon \sim 4.0$) due to the intraligand $\pi - \pi^*$ transition of the $N \stackrel{...}{-} C \stackrel{...}{-} S$ group [11–13]. The intraligand $\pi - \pi^*$ transition of the $S \stackrel{...}{-} C \stackrel{...}{-} S$ group, generally appears as a shoulder band and is associated with the unequal $C \stackrel{...}{-} S$ bonds of the ligand [14]. Thus in dithiocarbamate complexes this band is observed in cases where the dithiocarbamate moiety is bonded unequally to the metal ions or when the dithiocarbamate moiety is monodentate [12]. In the compounds studied here, although this band is observed in the ligand, sodium hexamethylenedithiocarbamate at 320 nm (log $\epsilon = 3.75$), it tends to disappear in the metal complexes, showing that the dithiocarbamate ligand is S–S bonded to the metal ions. This is in agreement with IR studies.

$La(C_6H_{12}NCS_2)_3$

The TG curve of this complex reveals that volatilization starts at 440 K and continues up to 1100 K, where no sample remains in the crucible of the thermobalance.

The DTA profile shows a broad endothermic peak with a T_{max} value of 439 K. This probably corresponds to the melting and volatilization of the complex.

$Pr(C_6H_{12}NCS_2)_3$

The TG curve indicates that volatilization begins at 495 K and continues up to 820 K, where no sample remains in the crucible of the thermobalance.

The DTA curve shows two endothermic peaks. The first thermal effect with $T_{max} = 491$ K is due to the melting of the complex. The endothermic peak with $T_{max} = 546$ K corresponds to the volatilization of the complex.

$Nd(C_6H_{12}NCS_2)_3$

The TG curve indicates that volatilization starts at 500 K and continues up to 860 K, where no sample remains in the crucible of the thermobalance.

An endothermic peak with $T_{max} = 499$ K corresponds to the melting of the complex. This is followed by another endothermic peak with $T_{max} = 542$ K due to the volatilization of the complex.

$Sm(C_6H_{12}NCS_2)_3$

It is observed from the TG curve that the volatilization of the complex starts at 410 K and continues up to 580 K, where no sample remains in the crucible of the thermobalance.

The DTA curve shows two endothermic peaks with T_{max} values of 405 K and 418 K. The former corresponds to the melting of the complex, whereas the latter is due to its volatilization.

$Tb(C_6H_{12}NCS_2)_3$

The TG curve of this complex reveals that volatilization begins at 400 K and continues up to 590 K, where no sample remains in the crucible of the thermobalance.

In the DTA curve the endothermic peak with $T_{max} = 393$ K corresponds to the melting of the complex. Its volatilization is shown by another endothermic peak with $T_{max} = 488$ K.

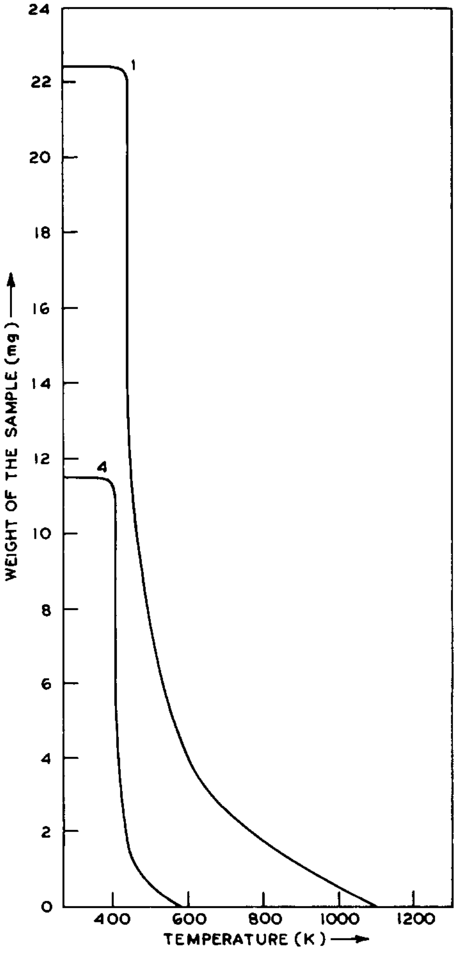

Fig. 1. TG curves: (1) $La(C_6H_{12}NCS_2)_3$; (4) $Sm(C_6H_{12}NCS_2)_3$.

TABLE 1

Thermal data

Complex	TG	DTA		
	Temp. range of volatilization (K)	Thermal effect	T_{max} (K)	ΔH (cal g^{-1})
$La(C_6H_{12}NCS_2)_3$	440–1100	Endothermic	439	–
$Pr(C_6H_{12}NCS_2)_3$	495– 820	Endothermic	491	–
		Endothermic	546	12.24
$Nd(C_6H_{12}NCS_2)_3$	500– 860	Endothermic	499	–
		Endothermic	542	35.48
$Sm(C_6H_{12}NCS_2)_3$	410– 580	Endothermic	405	–
		Endothermic	418	10.94
$Tb(C_6H_{12}NCS_2)_3$	400– 590	Endothermic	393	–
		Endothermic	488	9.16
$Dy(C_6H_{12}NCS_2)_3$	490– 780	Endothermic	488	–
		Endothermic	521	65.13

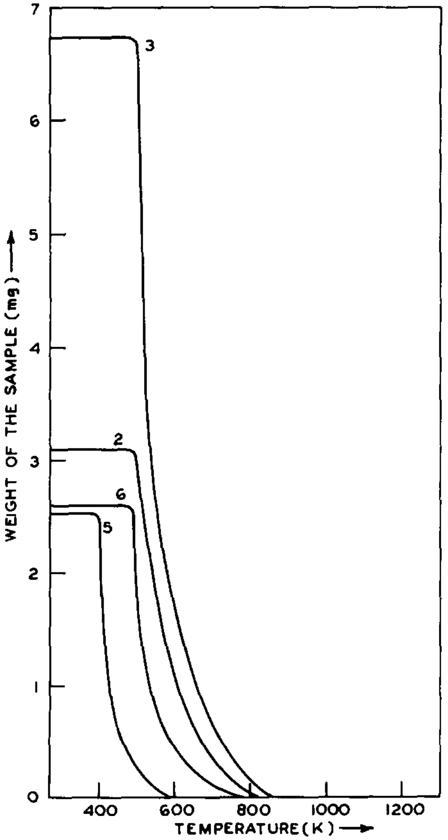

Fig. 2. TG curves: (2) $Pr(C_6H_{12}NCS_2)_3$; (3) $Nd(C_6H_{12}NCS_2)_3$; (5) $Tb(C_6H_{12}NCS_2)_3$; (6) $Dy(C_6H_{12}NCS_2)_3$.

Dy($C_6H_{12}NCS_2$)$_3$

The TG curve of this complex reveals that volatilization starts at 490 K and continues up to 780 K, where no sample remains in the crucible of the thermobalance.

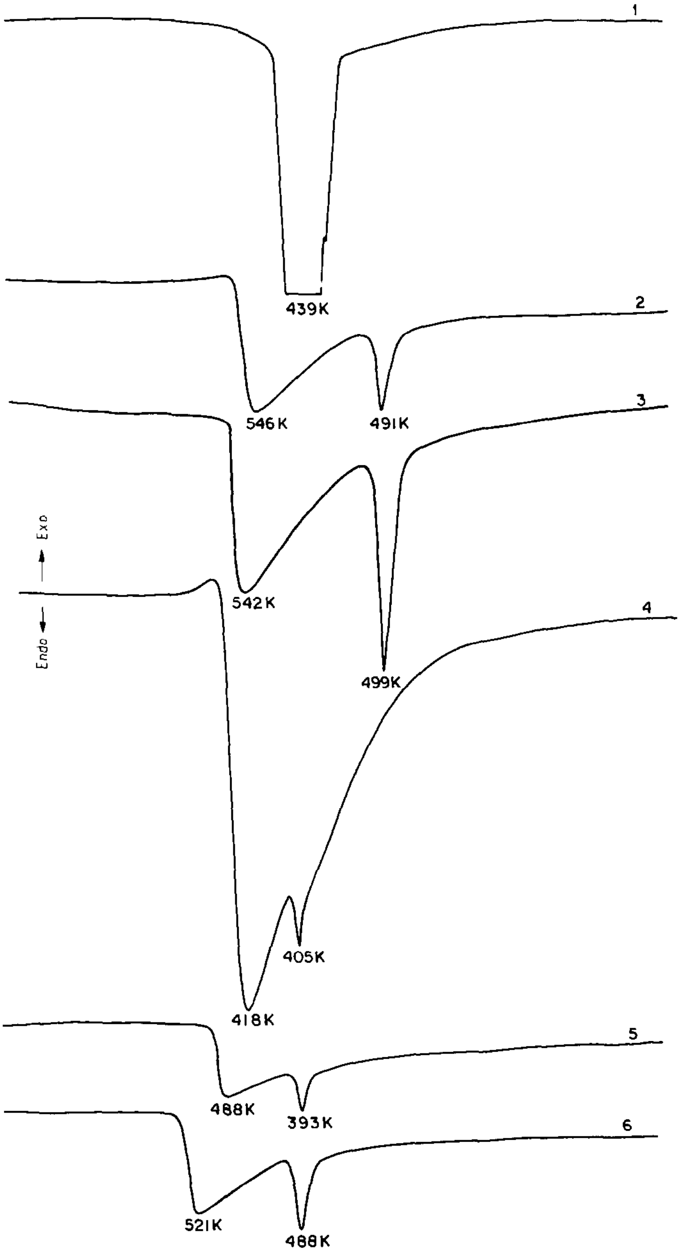

Fig. 3. DTA curves (1) La($C_6H_{12}NCS_2$)$_3$; (2) Pr($C_6H_{12}NCS_2$)$_3$; (3) Nd($C_6H_{12}NCS_2$)$_3$; (4) Sm($C_6H_{12}NCS_2$)$_3$; (5) Tb($C_6H_{12}NCS_2$)$_3$; (6) Dy($C_6H_{12}NCS_2$)$_3$.

In the DTA curve the endothermic peak with $T_{max} = 488$ K corresponds to the melting of the complex. This is followed by another endothermic peak with $T_{max} = 521$ K which corresponds to the volatilization of the complex.

The results of the TG and DTA evaluations are presented in Table 1. The TG curves are given in Figs. 1 and 2 and the DTA curves are presented in Fig. 3. From the DTA curves, the heat of vaporization ΔH was calculated [15] for the second thermal effect in each case, since the first peak corresponds to the melting of the complexes. The temperature-dependent calibration coefficient was obtained from the Currell equation [16]. The heat of vaporization ΔH was not calculated for $La(C_6H_{12}NCS_2)_3$ since a very broad thermal effect covering a wide range of temperature was observed. This precludes the calculation of ΔT_s.

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