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SYNTHESIS AND PHYSICO-CHEMICAL STUDIES ON NEODYMIUM(III) AND SAMARIUM (III) DERIVATIVES WITH MERCAPTO TRIAZOLES

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ABSTRACT

The reaction of $NdCl_3$ and $SmCl_3$ with 3-alkyl-4-amino-S-triazole-5-thiols, LH (alkyl = methyl/ethyl) and also with its Schiff bases L'H, L"H derived by the condensation of LH, with benzaldehyde, acetophenone and salicyaldehyde or o-hydroxyacetophenone have been carried out in aqueous ethanol. The products of types $[M(L_3)]\ 2H_2O$, $[M(L')_2Cl]$ and $[M(L")Cl(H_2O)_2]$ have been isolated and characterized by elemental analyses, electrical conductance, magnetic moment and spectral studies. The thermal behaviour of Nd(III) and Sm(III) complexes having only one series of ligand (L'H) and (L"H) were investigated by TG, DTG and DSC techniques. Kinetic parameters were determined by graphical method of Coats and Redfern. The heat of reaction for different decomposition steps was calculated from DSC curves.

INTRODUCTION

In recent years, the chemistry of transition metal complexes with sterically hindered heterocyclic ligands containing thioamide group $(-S = C- NH \rightleftharpoons NS-C = N-)$ continues to be of unabated interest on account of the stricking structural features presented by this class of compounds also because of their biological importance [1-8]. The present text reports the synthesis and characterization of Nd(III) and Sm(III) complexes with LH, L'H and L"H. The

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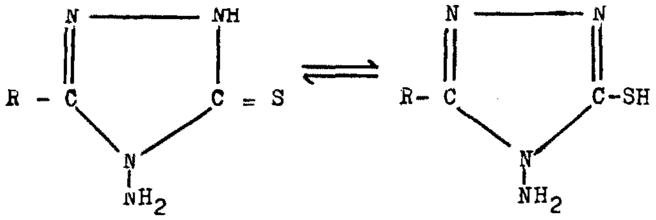
Structures of the ligands are shown below.

LH :

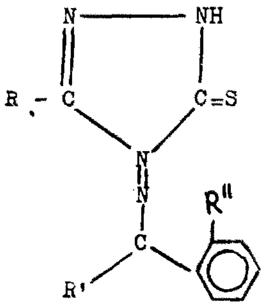


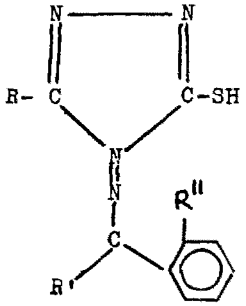
(Thione form) (Thiol form)

R= $CH_3(L_1H)$

R = $C_2H_5(L_2H)$

L'H and L"H :





where,

R'= H(L'H)

R"= OH(L"H)

R= CH_3, R'=H ($L_1'H$, $L_1''H$);

R= C_2H_5, R'=H ($L_2'H$, $L_2''H$);

R = CH_3, R'= CH_3 ($L_3'H$, $L_3''H$)

R = C_2H_5, R'= CH_3 ($L_4'H$, $L_4''H$)

EXPERIMENTAL

$NdCl_3$ and $SmCl_3$ were procured from BDH.

The preparations of ligands were done by the methods reported earlier [6, 9]. Metals were estimated as its oxide, chloride as AgCl, S as $BaSO_4$ and nitrogen by Kjeldahl method. Estimations of C and H were done at C.D.R.I., Lucknow. The details of physical measurements are the same as described earlier [10].

RESULTS AND DISCUSSION

The complexes are colored, amorphous in nature, soluble in all the common organic solvents. The molar conductance values are in the range of $10-25\ \Omega^{-1}\ cm^2\ mole^{-1}$, indicating their non-electrolytic behaviour in solution.

The magnetic moment values for Nd(III) and Sm(III) complexes lie in the range 3.40 - 3.58 and 1.40 - 1.58 B.M., respectively. These values indicate small deviations from Vanvleck values [11] and those of hydrated sulphates [12]. This suggests that 4f electrons do not take part in bonding due to very effective shielding by $5S^2\ 5p^6$ electrons.

The electronic absorption bands of Nd(III) and Sm(III) appear because of the transitions from the ground level $^4I_{9/2}$ and $^6H_{5/2}$ to the excited J levels of 4f configuration [13].

The assignment of IR spectral bands of ligands and the complexes is based on earlier studies on similar ligands [6-8]. In the complexes with the ligands LH and L'H, two bands are observed in the (C=N) (ring) frequency region: one band is located almost at the same position as observed for the ligands, but the other band is found located at lower frequency. This observation may be taken as an evidence for the co-ordination of metal with one of azomethine nitrogen.

THERMAL ANALYSIS

The thermal decomposition temperature range, DSC peak temperature and kinetic parameters(E, ΔH, and n) for different compounds have been reported in table I. The curves obtained from DSC measurements for all the complexes indicate that every thermal effect is accompanied by a corresponding mass loss. The complexes of type $[M(L)_3]_2H_2O$ and $[M(L'')Cl(H_2O)_2]$ show a three step weight loss, whereas $[M(L')_2Cl]$ shows a two step weight loss. The end products for all the complexes were found to be respective metal oxide (N_2O_3). The decomposition products at each step, for all the complexes, were confirmed by elemental analysis and IR spectra [14].

TABLE 1

Temperature ranges (^{o}C) of thermal decomposition and kinetic parameters

Compound	Decomposition	Temp. range ^{o}C	DSC peak tep.	E Kcal/ mole	ΔH Kcal/ mol.	n
$[Nd(L_1)_3]\cdot 2H_2O$	Dehydration	60-70	65	-	6.02	-
	Decomposition of dehydrated complex	230-370	300	38.15	54.21	Ist
	Decomposition of thiocyanate to oxide	480-510	480	-	70.16	-
$[Sm(L_1)_3]\cdot 2H_2O$	Dehydration	65-80	70	-	10.23	-
	Decomposition of dehydrated complex	250-400	340	40.24	48.94	Ist
	Decomposition of thiocyanate to oxide	485-520	485	-	7.81	-
$[Nd(L_1')_2Cl]$	Decomposition to oxychloride	250-360	300	27.12	94.22	Ist
	Decomposition of oxychloride to oxide	470-500	480	-	50.12	-
$[Sm(L_1')_2Cl]$	Decomposition to oxychloride	260-400	320	60.42	15.68	Ist
	Decomposition of oxychloride to oxide	480-520	490	-	55.25	-
$[Nd(L_3')_2Cl]$	Decomposition to oxychloride	265-360	300	35.28	9.14	Ist
	Decomposition of oxychloride to oxide	470-500	480	-	15.02	-

$[Sm(L_3')_2Cl]$	Decomposition of oxychloride oxide	270-380	320	42.15	22.32	Ist
	Decomposition of oxychloride to oxide	470-570	485	-	6.25	-
$[Nd(L_1'')Cl(H_2O)_2]$	Dehydration	160-175	170	-	15.33	-
	Decomposition of dehydrated complex to oxychloride	280-350	310	82.10	48.10	Ist
	Decomposition of oxychloride to oxide	460-510	480	-	9.33	-
$[Sm(L_1'')Cl(H_2O)_2]$	Dehydration	160-180	165	-	19.20	-
	Decomposition of dehydrated complex to oxychloride	290-375	340	37.15	40.20	Ist
	Decomposition of oxychloride to oxide	460-500	470	-	31.18	-
$[Nd(L_3'')Cl(H_2O)_2]$	Dehydration	170-180	170	-	16.18	-
	Decomposition of dehydrated complex to oxychloride	270-380	315	23.15	42.80	Ist
	Decomposition of oxychloride to oxide	460-510	480	-	18.22	-
$[Sm(L_3'')Cl(H_2O)_2]$	Dehydration	160-178	168	-	37.80	-
	Decomposition of dehydrated complex to oxychloride	275-390	315	21.25	6.48	Ist
	Decomposition of oxychloride to oxide	470-530	480	-	18.32	-

Calculation of the apparent activation energy and order of reaction were performed by employing the graphical method of Coats & Redfern [15]. The plot of $\left\{-\log\left[-\log(1-\alpha)/T^2\right]\right\}$ vs $\frac{1}{T} \times 10^3$ for n = 1.(n = order of reaction) gives a straight line with slope $-E/2.303\ R$.

Calculations for the heat of reaction from DSC curves was done by using the simple expression $\Delta H = KA/m$, where ΔH is heat of reaction, K is calibration constant, A is area under the peak and m is the mass of reactive compound.

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