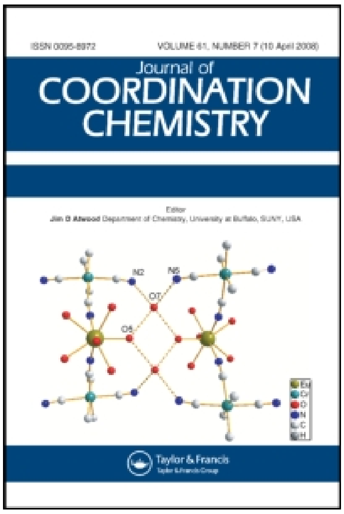

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SYNTHESIS AND PHYSICO-CHEMICAL STUDIES ON NEODYMIUM(III) AND SAMARIUM(III) COMPLEXES WITH TETRAAZA MACROCYCLIC LIGANDS

S. Goel[a]; U. K. Pandey[a]; O. P. Pandey[a]; S. K. Sengupta[a]
[a] Department of Chemistry, University of Gorakhpur, Gorakhpur, India

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SYNTHESIS AND PHYSICO-CHEMICAL STUDIES ON NEODYMIUM(III) AND SAMARIUM(III) COMPLEXES WITH TETRAAZA MACROCYCLIC LIGANDS

S. GOEL, U. K. PANDEY, O. P. PANDEY and S. K. SENGUPTA*

Department of Chemistry, University of Gorakhpur, Gorakhpur 273009, India

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Reactions of neodymium trichloride and samarium trichloride with 6,7,13,14-R_4–3,10-X_2-[14]-5,7,12,14-tetraene-1,5,8,12-N_4-[2,4,9,11-N_4] ($R = CH_3$, $X = 0$ ($L_1^{(1)}$); $R = C_6H_5$, $X = O$ ($L_1^{(2)}$); $R = CH_3$, $X = S$ ($L_2^{(1)}$)) and $R = C_6H_5$, $X = S$ ($L_2^{(2)}$)) have been studied in ethanol and complexes of the type $[M(L_1^{(1)}$ or $L_1^{(2)})]Cl_3$ and $[M(L_2^{(1)}$ or $L_2^{(2)})(H_2O)_2]Cl_3$ (M = Nd(III) and Sm(III)) have been isolated. In addition, macrocyclic complexes of Nd(III) and Sm(III) with another series of tetraaza ligands, *viz*, 5,6,11,12-R_4-3,8-X_2-[12]-4,6,10,12-tetraene-1,4,7,10-N_4-[2,9-N_2] ($R = CH_3$, $X = O$ ($L_3^{(1)}$); $R = C_6H_5$, $X = O$ ($L_3^{(2)}$); $R = CH_3$, $X = S$ ($L_4^{(1)}$); $R = C_6H_5$, $X = S$ ($L_4^{(2)}$)), formulated as $[M(L_3^{(1)}$, $L_3^{(2)}$, $L_4^{(1)}$ or $L_4^{(2)})(H_2O)_2]Cl_3$ (M = Nd(III) and Sm(III)) have been prepared by template condensation of Nd(III) and Sm(III) complexes of diacetylbis(semicarbazone/thiosemicarbazone) or benzilbis(semicarbazone/thiosemicarbazone) with diacetyl or benzil. The complexes have been identified by elemental analysis, electrical conductance, spectral and thermal measurements.

Keywords: Macrocycles, neodymium(III), samarium(III), synthesis, properties

INTRODUCTION

The intense interest in synthetic macrocycles and their metal complexes depends on the fact that they mimic naturally occurring macrocyclic molecules in their structural and functional features and on their rich chemical behaviour.[1,2] In addition, the study of metal complexes of macrocyclic ligands appears to be interesting in view of the possibility of obtaining coordination compounds of unusual structure and stability.[3–5] The formation of macrocyclic complexes depends on the dimension of the internal cavity, on the rigidity of the macrocycle, on the nature of its donor atoms and on the complexing properties of the anion involved in coordination.[1] Macrocyclic ligands are also of theoretical interest since they are capable of furnishing an environment of controlled geometry and ligand field strength.[6,7]

The coordination chemistry of polyaza macrocyclic ligands towards lanthanides has been little studied.[8–12] Recently, a few papers have appeared on crown ether and cryptand complexes of lanthanide ions, and it has been shown that they can be used for lanthanide separations, for stabilizing lower oxidation states and for promoting high coordination numbers in complexes of lanthanides(III).[13,14] The similarity between the ionic radii of calcium and the trivalent lanthanides and the remarkable spectroscopic and magnetic properties of the latter have led to the use of lanthanides in probing metal ion binding sites of biological interest including aminoacids, carbohydrates, nucleotides, sugar phosphates, porphyrins, phospholipids and membranes.

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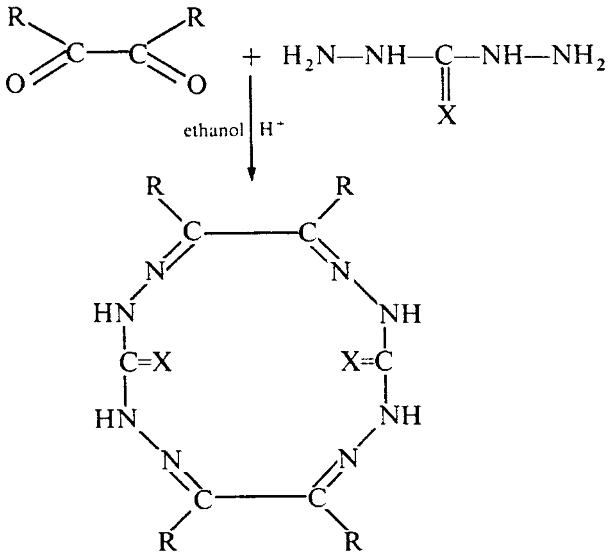
* Author for correspondence

In this paper we report the synthesis and characterization of neodymium(III) and samarium(III) macrocyclic complexes derived from the condensation of diacetyl or benzil with semicarbazide, thiosemicarbazide, carbohydrazide or thiocarbohydrazide.

RESULTS AND DISCUSSION

The condensation reactions of diacetyl or benzil with carbohydrazide or thiocarbohydrazide in ethanol in the presence of small amount of hydrochloric acid give rise to cyclic products shown below.



6,7,13,14-R_4-3,10-X_2[14]-5,7,12,14-tetraene-1,5,8,12-N_4-[2,4,9,11-N_4]

R	X	
CH_3	O	$L_1^{(1)}$
C_6H_5	O	$L_1^{(2)}$
CH_3	S	$L_2^{(1)}$
C_6H_5	S	$L_2^{(2)}$

These ligands react with neodymium(III) chloride and samarium(III) chloride in ethanol and the following two types of products have been isolated.

$$MCl_3 + L_1^{(1)}/L_1^{(2)} \xrightarrow{\text{ethanol}} [M\,(L_1^{(1)}/L_1^{(2)})]Cl_3$$

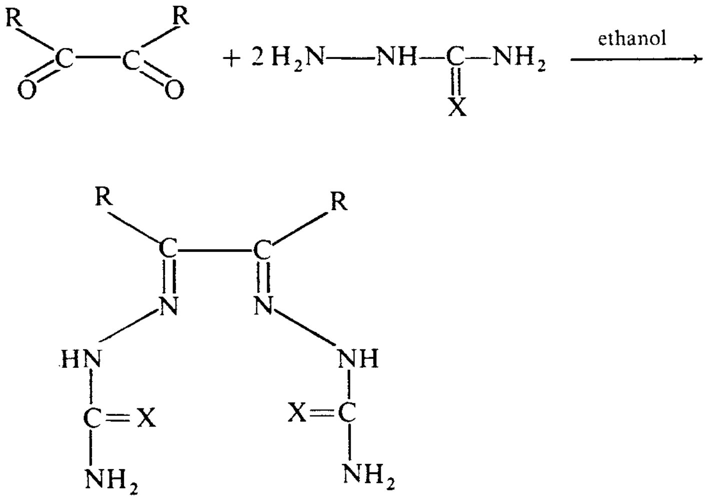
$$MCl_3 + L_2^{(1)}/L_2^{(2)} \xrightarrow{\text{ethanol}} [M\,(L_2^{(1)}/L_2^{(2)}(H_2O)_2)]Cl_3$$

TABLE I
Analytical data and magnetic moments for the complexes.

Complex	Colour	Found (Calcd.) %						μ_{eff}
		C	H	N	M	Cl	S	B.M.
$[Nd(L_1{}^{(1)})]Cl_3$	brown	22.4 (22.62)	2.8 (3.04)	21.1 (21.11)	27.0 (27.17)	20.0 (20.03)		3.42
$[Sm(L_1{}^{(1)})]Cl_3$	light brown	22.2 (22.37)	2.9 (3.00)	20.5 (20.87)	27.8 (28.0)	19.7 (19.81)		1.40
$[Nd(L_1{}^{(2)})]Cl_3$	yellowish-brown	46.2 (46.25)	3.0 (3.11)	14.1 (14.38)	18.4 (18.51)	13.2 (13.65)		3.60
$[Sm(L_1{}^{(2)})]Cl_3$	yellow	45.6 (45.89)	3.0 (3.08)	14.0 (14.27)	19.1 (19.15)	13.2 (13.54)		1.46
$[Nd(L_2{}^{(1)})(H_2O)_2]Cl_3$	brown	20.0 (20.05)	3.0 (3.37)	18.4 (18.71)	23.7 (24.08)	17.5 (17.76)	10.6 (10.7)	3.40
$[Sm(L_2{}^{(1)})(H_2O)_2]Cl_3$	yellowish-brown	19.5 (19.85)	3.1 (3.33)	18.2 (18.52)	24.8 (24.85)	17.1 (17.58)	10.6 (10.60)	1.50
$[Nd(L_2{}^{(2)})(H_2O)_2]Cl_3$	orange	42.3 (42.53)	3.0 (3.33)	13.1 (13.22)	17.0 (17.02)	12.2 (12.55)	7.2 (7.57)	3.48
$[Sm(L_2{}^{(2)})(H_2O)_2]Cl_3$	yellow	42.1 (42.22)	3.0 (3.31)	12.8 (13.13)	17.5 (17.61)	12.2 (12.46)	7.2 (7.51)	1.43
$[Nd(DAS)(H_2O)_2]Cl_3$	light brown	14.6 (14.80)	3.1 (3.31)	17.1 (17.26)	29.4 (29.63)	21.8 (21.85)		3.50
$[Sm(DAS)(H_2O)_2]Cl_3$	light brown	14.4 (14.62)	3.2 (3.27)	17.0 (17.05)	30.2 (30.50)	21.3 (21.58)		1.55
$[Nd(BZS)(H_2O)_2]Cl_3$	grey	31.2 (31.45)	3.3 (3.30)	13.2 (13.75)	23.5 (23.61)	17.4 (17.41)		3.40
$[Sm(BZS)(H_2O)_2]Cl_3$	light yellow	31.0 (31.14)	3.0 (3.27)	14.1 (14.43)	23.9 (24.36)	17.1 (17.24)		1.48
$[Nd(DATS)(H_2O)_2]Cl_3$	pink	13.5 (13.89)	3.0 (3.11)	16.0 (16.19)	27.5 (27.79)	20.3 (20.49)	12.2 (12.36)	3.60
$[Sm(DATS)(H_2O)_2]Cl_3$	light brown	13.5 (13.73)	3.0 (3.07)	16.0 (16.00)	28.4 (28.63)	20.0 (20.26)	12.1 (12.21)	1.42
$[Nd(BZTS)(H_2O)_2]Cl_3$	light brown	29.7 (29.60)	3.0 (3.11)	13.1 (12.94)	22.1 (23.16)	16.2 (16.38)	9.8 (9.88)	3.58
$[Sm(BZTS)(H_2O)_2]Cl_3$	yellowish-brown	29.6 (29.60)	3.0 (3.11)	12.6 (12.94)	23.0 (23.16)	16.1 (16.38)	9.8 (9.88)	1.50
$[Nd(L_3{}^{(1)})(H_2O)_2]Cl_3$	dark brown	22.1 (22.37)	3.2 (3.38)	15.4 (15.65)	26.6 (26.87)	19.5 (19.81)		3.47
$[Sm(L_3{}^{(1)})(H_2O)_2]Cl_3$	dark brown	22.0 (22.12)	3.3 (3.34)	15.2 (15.48)	27.4 (27.69)	19.2 (19.59)		1.46
$[Nd(L_3{}^{(2)})(H_2O)_2]Cl_3$	dark yellow	45.7 (45.89)	3.0 (3.34)	10.6 (10.70)	18.2 (18.37)	13.5 (13.55)		3.45
$[Sm(L_3{}^{(2)})(H_2O)_2]Cl_3$	dark brown	45.3 (45.54)	3.1 (3.31)	10.5 (10.62)	19.0 (19.00)	13.4 (13.44)		1.45
$[Nd(L_4{}^{(1)})(H_2O)_2]Cl_3$	dark brown	21.0 (21.11)	3.1 (3.19)	14.4 (14.77)	25.0 (25.35)	18.2 (18.69)	11.0 (11.27)	3.55
$[Sm(L_4{}^{(1)})(H_2O)_2]Cl_3$	dark yellow	20.6 (20.88)	3.0 (3.15)	14.4 (14.61)	26.0 (26.14)	18.3 (18.49)	11.0 (11.15)	1.43
$[Nd(L_4{}^{(2)})(H_2O)_2]Cl_3$	brownish-yellow	44.8 (45.09)	3.2 (3.21)	10.1 (10.28)	17.6 (17.65)	13.0 (13.01)	7.6 (7.85)	3.50
$[Sm(L_4{}^{(2)})(H_2O)_2]Cl_3$	violet	43.6 (43.76)	3.0 (3.18)	10.1 (10.21)	18.2 (18.26)	12.8 (12.92)	7.7 (7.79)	1.54

The elemental analyses of the complexes reveal 1 : 1 metal to ligand stoichiometry (Table I). The purity of the complexes was checked by TLC. The complexes are found to be soluble in ethanol, dimethylformamide, dimethylsulphoxide and sparingly soluble in chloroform. The electrical conductances in dimethylformamide indicate 1 : 3 electrolytic behaviour. The presence of coordinated water molecules in the second type of complex was inferred by thermogravimetric analysis which indicates the loss of two water molecules at 160–180°C.

However, diacetyl or benzil react with semicarbazide or thiosemicarbazide at a 1 : 2 molar ratio, respectively, and form the ring opened ligands shown below.



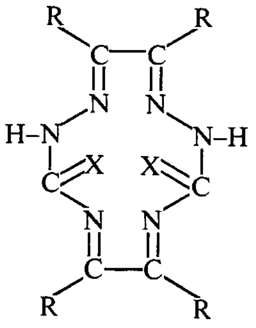
R	X	
CH_3	O	Diacetyl bis(semicarbazone); (DAS)
C_6H_5	O	Benzil bis(semicarbazone); (BZS)
CH_3	S	Diacetyl bis(thiosemicarbazone); (DATS)
C_6H_5	S	Benzil bis(thiosemicarbazone); (BZTS)

These ligands react with neodymium(III) and samarium(III) chloride to form ring-opened complexes.

$$MCl_3 + DAS/BZS \longrightarrow [M(DAS/BZS(H_2O)_2]Cl_3$$

$$MCl_3 + DATS/BZTS \longrightarrow [M(DATS/BZTS)(H_2O)_2]Cl_3$$

It appears that in the above complexes the two terminal amino groups remain uncoordinated and can take part in condensation reactions with α-diketones and therefore reactions of the above complexes with diacetyl or benzil have been carried out which result in the formation of complexes with the following ligands.



5,6,11,12-R_4-3,8-X_2-[12]-4,6,10,12-tetraene-1,4,7,10-N_4-[2,9 N_2]

R	X	
CH_3	O	$L_3^{(1)}$
C_6H_5	O	$L_3^{(2)}$
CH_3	S	$L_4^{(1)}$
C_6H_5	S	$L_4^{(2)}$

The metal to ligand stoichiometry of these macrocyclic products has been established on the basis of elemental analyses (Table I). The presence of coordinated water molecules was inferred by thermogravimetric study (weight loss at 160–180°C corresponds to two water molecules). These complexes have high melting points and are soluble in dimethylformamide and dimethylsulphoxide. The complexes behave as 1 : 3 electrolytes in dimethylformamide. Since the cyclic products derived from semicarbazide and thiosemicarbazide could not be isolated in the absence of metal ion, neodymium(III) or samarium(III) ions appear to act as kinetic "templates".

Magnetic Moment and Electronic Spectra

The magnetic moments for the neodymium(III) and samarium(III) complexes lie in the range 3.40–3.60 and 1.40–1.55 B.M., respectively. However, the values show little deviation from Van Vleck values[15] and those of hydrated sulphates.[16] This indicates that the 4f electrons do not take part in bonding, due to very effective shielding by the $5s^25p^6$ electrons.

Since electrons in the 4f orbitals are well shielded from the ligand field by the intervening $5s^25p^6$ octet, the order of perturbations for a lanthanide ion is crystal field < spin-orbit coupling < interelectronic repulsions. Thus, the line-like absorption spectra of the neodymium and samarium chelates arise from electronic transitions within the 4f levels, which are normally forbidden but allowed after the removal of degeneracy in the 4f orbitals by external crystal fields. Neodymium(III) complexes show bands around 11500–12000, 12800–12900, 13000–13200, 13500–14000, 18500–18700, 19500, 20000–20800 and 23000–23500 cm^{-1}, assignable[17] to transitions from the $^4I_{9/2}$ level to the $^4F_{5/2}$, $^2H_{9/2}$, $^4F_{7/2}$, $^2S_{3/2}$, $^4G_{7/2}$, $^2G_{9/2}$, $^4G_{9/2}$, $^2P_{1/2}$ energy levels, respectively. Samarium(III) complexes show bands around 17200–17500, 18500–18900, 20000–20200, 20500–20700, 21500–22000, 23800, 25000–

25300 cm^{-1} corresponding to the transitions from ${}^6H_{5/2}$ to ${}^4G_{5/2}$, ${}^4F_{3/2}$, ${}^4G_{7/2}$, ${}^4I_{9/2}$, ${}^4I_{13/2}$, ${}^6P_{5/2}$, and ${}^4F_{9/2}$, energy levels, respectively.

It has been observed that on complexation the electronic spectral bands of Nd(III) and Sm(III) shift to lower energy. The slight shifts in the bands have been attributed by Jørgensen[18] to the effect of crystal fields upon the interelectronic repulsions between the 4f electrons (*i.e.* to lowering of the interelectronic repulsion parameter in the complexes). Further, a marked enhancement in the intensity of the bands upon complexation is also observed. Values of the nephelauxetic ratio (β), defined as ν_c/ν_t where ν_c and ν_t are the energies (in cm^{-1}) of the transitions in the complexed and free ion for Nd(III) and Sm(III) derivatives, lie in the range 0.9870–0.9920 and 0.9810–0.9880, respectively. From the mean β values, the covalency parameters (δ) and bonding parameter ($b^{1/2}$) were determined using the standard procedure.[18,20] The values of δ for Nd(III) and Sm(III) derivatives lie in the range 0.950–1.450 and 1.402–1.950, respectively. The values of $b^{1/2}$ for Nd(III) and Sm(III) complexes lie in the range 0.0630–0.0845 and 0.0890–0.0970, respectively. The values of β, which are less than unity, and positive values of δ and $b^{1/2}$ support partial covalent bonding between metal and ligand. The magnitudes of the covalency and bonding parameters increase from Nd(III) to Sm(III) indicating that the extent of the covalent character of the metal–ligand bond increases with increase in atomic number which is in conformity with the lanthanide contraction.

Infrared Spectra

Complexes with $L_1^{(1)}$, $L_1^{(2)}$, $L_2^{(1)}$ and $L_2^{(2)}$

The infrared spectra of the macrocyclic ligands derived from condensation of carbohydrazide with diacetyl or benzil ($L_1^{(1)}$ and $L_1^{(2)}$) show bands at *ca* 1675, 1500, 1260 and 660 cm^{-1} which may be assigned[21–23] to amide I (νC=O), amide II (νC–N + δN–H), amide III (δN–H) and amide IV (φC=O) vibrations, respectively. In the neodymium(III) and samarium(III) complexes all of these bands (except amide I) show an upward shift ($\sim$60–40 cm^{-1}), whereas the amide I band shows a downward shift ($\sim$30 cm^{-1}). These changes in amide group vibrations indicate[21] that the amide oxygens (ketonic) take part in coordination to the metal atom. This has been further confirmed by the appearance of a band at *ca* 520–480 cm^{-1} in the complexes, assigned to ν(M–O). The infrared spectra of macrocyclic ligands derived by the condensation of thiocabohydrazide with diacetyl or benzil ($L_2^{(1)}$ and $L_2^{(2)}$) show bands at *ca* 1560, 1210, 1080 and 765 cm^{-1}, which are assigned[24,25] to thioamide I, II, III and IV vibrations, respectively. The ligands containing the HN–C=S group can undergo thione $\leftrightarrows$ thiol tautomerism. However, the appearance of four thioamide bands in the spectra of the ligands indicates[24] the existence of ligands in the thione form. The thioamide IV band has been found to have maximum νC=S contribution. However, in the neodymium(III) and samarium(III) complexes all bands persist at the same position indicating that the thiocarbonyl group is not bonded to the metal atom.

In addition, all these types of ligands show a weak band at *ca* 1640 cm^{-1} which can be assigned to the ν(C=N) vibration of the azomethine linkage. The appearance of a weak ν(C=N) band is in accordance with the observations of several other workers.[26,27] In the neodymium(III) and samarium(III) complexes the band appears at *ca* 1620–1610 cm^{-1} suggesting the coordination of azomethine nitrogens to the metal atom. The ν(M–N) vibration band is observed at *ca* 400–380 cm^{-1} in the complexes.

The infrared spectra of the neodymium(III) and samarium(III) complexes with ligands $L_2^{(1)}$ and $L_2^{(2)}$ show broad bands at *ca* 3480–3420 cm^{-1} which are assigned to the ν(O–H) vibration of the coordinated water molecule.

A number of other bands also arise due to the phenyl and methyl groups but definite assignments are not possible. It may therefore be concluded that ligands of type $L_1^{(1)}$ and $L_1^{(2)}$ act as hexadentates through four azomethine nitrogen and two amide oxygen atoms. Ligands of type $L_2^{(1)}$, $L_2^{(2)}$ act as tetradentates through four azomethine nitrogen atoms.

Complexes with DAS, BZS, DATS, BZTS

The ligands DAS and BZS show bands due to the amide, amino and azomethine groups. The bands at *ca* 1650, 1500, 1250 and 650 cm^{-1} may be assigned[21] to amide I, amide II, amide III and amide IV vibrations, respectively, as with ligands $L_1^{(1)}$ and $L_1^{(2)}$. In the neodymium(III) and samarium(III) complexes the amide I band shows a downward shift (~40–20 cm^{-1}). These changes indicate[21] that amide oxygen (ketonic) takes part in coordination to the metal atom. The (M–O) vibration appears at *ca* 500–480 cm^{-1}. The ligands also show a weak band at *ca* 1630–1625 cm^{-1} assignable[26,27] to ν(C=N) of the azomethine linkage. In the complexes this band shifts to lower frequency (*ca* 30–20 cm^{-1}) suggesting that the nitrogen atoms of the azomethines are coordinated to the metal atom. This is further supported by the appearance of weak band at *ca.* 400–380 cm^{-1} assignable to ν(M–N). The ligands DAS and BZS also show a broad band at 3280 cm^{-1} along with two shoulders at 3300 and 3260 cm^{-1}, which may be due to ν_{sym} (N–H) and ν_{asym} (N–H) vibrations. In the complexes all these bands persist indicating that the terminal amino group is not bound to the metal.

The ligands DATS and BZTS show bands due to thioamide, amino and azomethine groups. The four thioamide bands appear at *ca* 1570–1550, 1210, 1080–1070 and 760 cm^{-1}. The thioamide IV band undergoes shifts to lower frequency (~35–20 cm^{-1}) in the complexes, indicating[24,28] the coordination of sulphur to the metal. The new band in the complexes at *ca* 360–320 cm^{-1} may be assigned to ν(M–S). A weak band in the spectra of DATS and BZTS appears at *ca* 1630 cm^{-1} and is assignable[26] to ν(C=N). In the complexes this band also shifts to lower frequency (~25 cm^{-1}) indicating the coordination of azomethine nitrogens to the metal atom. The amino group vibrations appear at 3280 cm^{-1}, 3250 cm^{-1} (shoulder) and 3220 cm^{-1} (shoulder). In the neodymium and samarium complexes these bands appear exactly at the same position indicating the non-coordination of the terminal amino groups to the metal atom. All the complexes show broad bands at *ca* 3440 cm^{-1} suggesting the presence of coordinated water molecules.

It is thus apparent that DAS, BZS, DATS and BZTS act as tetradentates *via* two azomethine nitrogens and two amide oxygen atoms (DAS or BZS) or two thioamide sulphur atoms (DATS or BZTS).

Complexes with $L_3^{(1)}$, $L_3^{(2)}$, $L_4^{(1)}$ and $L_4^{(2)}$

The neodymium(III) and samarium(III) complexes with DAS, BZS, DATS and BZTS contain terminal amino groups (*vide supra*), which may participate in nucleophilic condensation reactions with α-diketones. Thus, the reactions of complexes of

DAS, BZS, DATS, BZTS with diacetyl or benzil were carried out in the presence of glacial acetic acid, causing the ring closure and formation of cyclic products with the macrocyclic ligands $L_3^{(1)}$, $L_3^{(2)}$, $L_4^{(1)}$, $L_4^{(2)}$. The infrared spectra of the cyclic products show the same pattern of bands for the amide ($L_3^{(1)}$ and $L_3^{(2)}$, thioamide ($L_4^{(1)}$ and $L_4^{(2)}$) and azomethine groups. This indicates that in the macrocyclic complexes with $L_3^{(1)}$ and $L_3^{(2)}$ the ligand is bonded to the metal atom through two azomethine nitrogen and two ketonic oxygen atoms. Similarly, in the complexes with $L_4^{(1)}$ and $L_4^{(2)}$, the ligands are coordinated to the metal through two thioamide sulphur and two azomethine nitrogen atoms. However, in both types of complexes, the (νNH_2) band disappears. Only one band is observed in the $\nu N\text{–}H$ region at 3200 cm^{-1} (due to a secondary amino group), thus establishing the condensation of the primary amino groups with the carbonyl groups of the α-diketones. This is further supported by the appearance of a weak band at *ca* 1650–1635 cm^{-1}, due to the formation of azomethine linkages. The complexes with these ligands also contain coordinated water molecules, as is evident by the presence of a broad band at *ca* 3480 cm^{-1} in the infrared spectra.

Proton Magnetic Resonance Spectra

The ^1H NMR spectra (90 MHz) of the complexes with Ligands $L_1^{(1)}$, $L_1^{(2)}$, $L_2^{(1)}$, $L_2^{(2)}$, $L_3^{(1)}$, $L_3^{(2)}$, $L_4^{(1)}$, $L_4^{(2)}$, obtained in deuterated chloroform or in DMSO-d_6 solution with TMS as internal standard show the methyl protons at *ca* δ 2.2–2.8 ppm and phenyl protons at *ca* δ 6.8–7.2 ppm. These signals are shifted downfield as compared to the corresponding signals of the free ligands.

Thermal Analysis

The thermal stability and decomposition ranges of the neodymium(III) and samarium(III) complexes with ligands $L_1^{(1)}$, $L_1^{(2)}$, $L_2^{(1)}$, $L_2^{(2)}$, $L_3^{(1)}$, $L_3^{(2)}$, and $L_4^{(1)}$, $L_4^{(2)}$, in air are given in Table II. There is a qualitative 1 : 1 correspondence between the DSC and DTG curves for all these complexes, indicating that every thermal effect is accompanied by a corresponding mass loss.

Complexes of the type $[M(L_1^{(1)}$ or $L_1^{(2)})]Cl_3$

The TG and DTG curves of $[M(L_1^{(1)}$ or $L_1^{(2)})]Cl_3$ show a two-step weight loss. The first step occurs at 225–380°C and corresponds to loss of the organic ligands. At the end of first step, the respective metal oxychloride is formed. The DSC curve also shows an endothermic peak in this temperature range. The metal oxychloride is stable up to 450°C and then undergoes decomposition (450–530°C) to give the metal oxide. The formation of the metal oxide is observed as a single endothermic peak. The formation of metal oxychloride and oxide was confirmed by elemental analysis and IR spectra.[29]

Complexes of the type $[M(L_2^{(1)}, L_2^{(2)}, L_3^{(1)}, L_3^{(2)}, L_4^{(1)}$ or $L_4^{(2)})(H_2O)_2]Cl_3$

All these complexes show similar patterns of decomposition with three weight losses. The first loss occurs at 160–180°C corresponding to the loss of two water molecules and was shown by DSC to be endothermic. The dehydrated complex was stable up to ~250°C and then (~250–400°C) decomposes to give metal oxychloride endothermically. The metal oxychloride then decomposes at 450–520°C and the metal oxide is formed. The intermediate and final products were again characterized by elemental analyses and infrared spectra.[29] Neodymium(III) complexes are found to be less stable than their corresponding sarmarium(III) complexes.

TABLE II
Thermal decomposition ranges and kinetic parameters for the complexes.

Compound	Reaction	Temp. range (°C)	DSC peak temp.	Activation energy (kJ mol^{-1})	Heat of reaction (kJ mol^{-1})
$[Nd(L_1^{(1)})]Cl_3$	decomposition to oxychloride	250–360	285	177.0	251.5
	decomposition of oxychloride to oxide	450–520	480		92.7
$[Sm(L_1^{(1)})]Cl_3$	decomposition to oxychloride	260–380	300	233.5	126.7
	decomposition of oxychloride to oxide	460–530	500		201.3
$[Nd(L_1^{(2)})]Cl_3$	decomposition to oxychloride	225–340	275	115.1	176.5
	decomposition of oxychloride to oxide	450–490	460		45.8
$[Sm(L_1^{(2)})]Cl_3$	decomposition to oxychloride	245–370	320	201.3	243.5
	decomposition of oxychloride to oxide	470–520	500		78.0
$[Nd(L_2^{(1)})(H_2O)_2]Cl_3$	dehydration	165–175	170		42.5
	decomposition to oxychloride	250–350	310	295.7	219.2
	decomposition of oxychloride to oxide	450–490	460		85.4
$[Sm(L_2^{(1)})(H_2O)_2]Cl_3$	dehydration	170–180	170		28.5
	decomposition to oxychloride	280–380	340	335.9	252.7
	decomposition of oxychloride to oxide	480–520	510		66.0
$[Nd(L_2^{(2)})(H_2O)_2]Cl_3$	dehydration	160–170	160		53.3
	decomposition to oxychloride	250–350	310	166.9	159.8
	decomposition of oxychloride to oxide	465–500	480		89.4
$[Sm(L_2^{(2)})(H_2O)_2]Cl_3$	dehydration	165–180	170		81.9
	decomposition to oxychloride	290–400	345	214.3	168.6
	decomposition of oxychloride to oxide	485–520	510		102.5
$[Nd(L_3^{(1)})(H_2O)_2]Cl_3$	dehydration	160–178	168		65.6
	decomposition to oxychloride	258–342	282	251.7	111.6
	decomposition of oxychloride to oxide	455–500	485		86.6
$[Sm(L_3^{(1)})(H_2O)_2]Cl_5$	dehydration	162–180	170		79.0
	decomposition to oxychloride	275–400	380	285.4	127.5
	decomposition of oxychloride to oxide	460–510	490		113.8
$[Nd(L_3^{(2)})(H_2O)_2]Cl_3$	dehydration	160–175	160		78.7
	decomposition to oxychloride	280–350	320	125.4	183.3
	decomposition of oxychloride to oxide	460–510	475		92.0
$[Sm(L_3^{(2)})(H_2O)_2]Cl_3$	dehydration	160–180	170		61.0
	decomposition to oxychloride	295–400	350	142.5	229.9
	decomposition of oxychloride to oxide	480–520	480		111.2
$[Nd(L_4^{(1)})(H_2O)_2]Cl_3$	dehydration	160–180	170		51.8
	decomposition to oxychloride	250–370	325	272.9	201.7
	decomposition of oxychloride to oxide	450–490	478		76.2
$[Sm(L_4^{(1)})(H_2O)_2]Cl_3$	dehydration	160–180	175		77.7
	decomposition to oxychloride	280–400	348	334.7	249.7
	decomposition of oxychloride to oxide	465–515	492		93.8
$[Nd(L_4^{(2)})(H_2O)_2]Cl_3$	dehydration	162–178	165		70.3
	decomposition to oxychloride	258–390	320	316.6	253.0
	decomposition of oxychloride to oxide	460–500	488		86.0
$[Sm(L_4^{(2)})(H_2O)_2]Cl_3$	dehydration	165–180	172		76.5
	decomposition to oxychloride	278–400	338	355.4	261.8
	decomposition of oxychloride to oxide	482–520	505		89.2

Calculation of the apparent activation energy and order of reaction was performed by employing the graphical method of Coats and Redfern.[30] The plot of $\{-\log[-\log(1-\alpha)/T^2]\}$ *vs* $\frac{1}{T} \times 10^3$ for $n = 1$ (n = order of reaction) gives a straight line with slope $-E/2.303\,R$. Calculation of the heat of reaction from DSC curves made use of the expression $\Delta H = KA/m$ where ΔH is the heat of reaction, K is a calibration constant, A is the area under peak and m is the mass of the reactive compound. The calibration constant K was calculated by using the equation

$$K = \frac{\Delta H\, m\, c}{A\, \Delta T_s}$$

where c is chart speed and ΔT_s is the temperature sensitivity. To calibrate the DSC instrument, pure indium metal was used. The apparent activation energies and heats of reaction are given in Table II.

EXPERIMENTAL

Neodymium(III) and samarium(III) chloride were obtained from British Drug Houses Ltd., and were estimated gravimetrically as oxides. Sulphur was determined as $BaSO_4$ and nitrogen by the Kjeldehl method in the complexes. Estimation of carbon and hydrogen was done by CDRI, Lucknow. The ligands $L_1^{(1)}$, $L_1^{(2)}$, $L_2^{(1)}$, $L_2^{(2)}$, DAS, BZS, DATS, BZTS were prepared as reported earlier.[20,31,32] The details of physical measurements are the same as those described earlier.[21]

TG and DTG curves were recorded simultaneously on a SETARAM G-70 thermoanalyser with sample size 26–36 mg, heating rate 8 K min^{-1} and flow rate of gas 10 cm^3 m^{-1}. The DSC curves were recorded on a Perkin-Elmer DSC-1 instrument using 10 mg samples.

Preparation of complexes with $L_1^{(1)}$, $L_1^{(2)}$, $L_2^{(1)}$ or $L_2^{(2)}$

Neodymium(III) or samarium(III) chloride (0.02 mol) in water (20 cm^3) was added to a refluxing solution of the appropriate ligand (0.02 mol) in ethanol (30 cm^3). The reaction mixture was refluxed for 8–10 hrs, when the colour of the solution turned yellowish brown. The solvent was removed *in vacuo* and a brown or yellowish-brown product was obtained. The product was thoroughly washed with dichloromethane to remove impurities and dried *in vacuo*. Yield ~45–50%.

Preparation of complexes with DAS, BZS, DATS or BZTS

Neodymium(III) or samarium(III) chloride (0.02 mol) dissolved in water was added to the appropriate ligand (0.02 mol) dissolved in a mixture of benzene and ethanol (1 : 2, 30 cm^3). For the preparation of complexes with DATS or BZTS, a small amount of alkali (30%, 5 cm^3) was also added. The solution was refluxed for 10–14 hrs. The solvent was removed *in vacuo* and a light-brown product was obtained. The complex was recrystallized from tetrahydrofuran. Yield ~65–68%.

Preparation of complexes with $L_3^{(1)}$, $L_3^{(2)}$, $L_4^{(1)}$, $L_4^{(2)}$

Diacetyl or benzil (0.01 mol) in ethanol (15 cm^3) was added to the complexes of neodymium or samarium with DAS, BZS, DATS or BZTS dissolved in a mixture of benzene and ethanol (1 : 1, 30 cm^3). Glacial acetic acid (5 cm^3) was added to the mixture and a clear solution (pH $\sim$ 3) was obtained which was refluxed for 7–8 hrs, when dark brown precipitates were obtained. The precipitates were filtered, thoroughly washed with benzene and ethanol and dried *in vacuo*. Yield 45–55%

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