

Synthesis, Physico-Chemical and Thermal Characteristics of Seven and Ten Coordinated Complexes of Trivalent Lanthanides Derived from 4[N-(cinnamalidene)amino]antipyrine Semicarbazone and Diphenyl Sulfoxide

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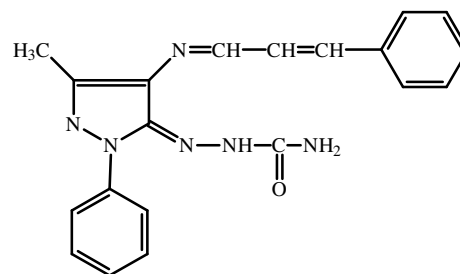
In present studies a new series of twenty four complexes of seven and ten coordinated compounds derived from 4[N-(cinnamalidene)amino]antipyrine semicarbazone (CAAPS) as primary ligand and diphenyl sulfoxide (DPSO) as secondary ligand has been reported. All the complexes have the general composition $\text{LnX}_{3.n}(\text{CAAPS})_n(\text{DPSO})_n$ ($\text{Ln} = \text{La, Pr, Nd, Sm, Gd, Tb, Dy}$ or Ho , $\text{X} = \text{NCS}$ or ClO_4 , $n = 2$, $\text{X} = \text{NO}_3$, $n = 1$). The compounds have been characterized by elemental analysis, molar conductance, magnetic susceptibility, infrared and electronic spectra. Thermal characteristics were also reported. Based on the data appropriate structures are assigned for these complexes.

Keywords: Lanthanide(III), Complexes, 4[N-Cinnamalidene)amino]antipyrine semicarbazone, Diphenyl sulfoxide

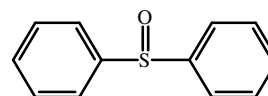
INTRODUCTION

The structural chemistry of the lanthanide compounds has recently undergone considerable development and a wide variety of coordination numbers and geometries have been observed. Because of their larger size, the lanthanide ions generally gave higher coordination numbers than transition elements [1-5]. Typical coordination numbers for transition metal ions are 4 and 6, the coordination being square planar, tetrahedral or octahedral. Coordination numbers greater than 6 are not common for transition elements. On the other hand lanthanide ions with their high positive charge and larger size are the best candidates to form stable complexes with high coordination numbers and generally coordination numbers of 6 to 10 are observed [1-5]. In the present study, we report the synthesis and physico-chemical properties of some seven and ten coordinated complexes of trivalent lanthanides derived

from 4[N-(cinnamalidene)amino]antipyrine semicarbazone (CAAPS) as primary ligand and diphenyl sulfoxide (DPSO) as secondary ligand.



CAAPS



DPSO

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EXPERIMENTAL

The lanthanide nitrates and oxides were obtained from Rare Earth Products Ltd. (India) and used without further purification. The lanthanide perchlorates were prepared by heating the corresponding oxides with perchloric acid and evaporating off the excess of solid [6]. The lanthanide isothiocyanates were prepared by adding a warm ethanolic solution of lanthanide nitrate to warm ethanolic solution of KCNS. The precipitate of KNO_3 rapidly coagulated. The volume of the solution was reduced on a water bath, cooled, filtered and the filtrate was used for complexation [7]. The ligand CAAPS was synthesized in the laboratory by a reported method [8]. Diphenyl sulfoxide (DPSO) was obtained from Merck. The solvents used in this studies was purchased from SD-chemicals and used as such or after distillation if felt necessary.

Synthesis of the Complexes

(i) **$\text{Ln}(\text{NO}_3)_3 \cdot (\text{CAAPS}) \cdot \text{DPSO}$ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho).** All the lanthanide(III) nitrate complexes of CAAPS and DPSO were synthesized by the following method. The corresponding metal salt (1 mmol) was dissolved in dry ethanol (15 ml) and added to the refluxing solution of the ligand (CAAPS) (1 mmol) and DPSO (1 mmol) in dry ethanol (20 ml). The reaction mixture was refluxed for ~2 h, when a coloured mass separated out. The precipitate was filtered off, washed with ethanol and dried *in vacuo* over P_4O_{10} .

(ii) **$\text{Ln}(\text{NCS})_3 \cdot 2(\text{CAAPS}) \cdot \text{DPSO}$ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho).** All the complexes were synthesized as follows: A methanolic solution of the ligands CAAPS (2 mmol) and DPSO (1 mmol) was refluxed for 1 h, and then a methanolic solution of the trivalent lanthanide isothiocyanate (1 mmol) was added. The reaction mixture was refluxed for ~2 h and then kept for slow heating on the hot plate till a thick layer of the precipitate settled down. The supernatant liquid was decanted off and the product was dried off. It was then washed several times with methanol to remove any excess of metal ions/and or ligand. Finally, the complexes were dried *in vacuo* over P_4O_{10} .

(iii) **$\text{Ln}(\text{ClO}_4)_3 \cdot 2(\text{CAAPS}) \cdot \text{DPSO}$ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho).** All the titled complexes of CAAPS and

DPSO were synthesized by the following method. The corresponding metal salt (1 mmol) was taken in anhydrous ethanol (1 ml) and added to the refluxing solution of CAAPS (2 mmol) and DPSO (1 mmol) in anhydrous ethanol (20 ml). The reaction mixture was refluxed for ~2-3 h, when a coloured mass separated out. The precipitate was filtered off, washed with ethanol and ether and dried as above.

Physico-Chemical Techniques

The lanthanide metal contents were estimated as its oxide by direct combustion in a platinum crucible. The estimation was further confirmed by dissolving the product of direct combustion in dilute HCl. The acid extract was transferred into a flask, pH was adjusted to 5.8-6.4 by the addition of acetic acid-sodium acetate buffer and was then titrated against 0.1 M EDTA using xylenol-orange as an indicator. The results from both methods were compared and found within the experimental errors. Nitrogen was determined in the laboratory by the kjeldahl method, while sulfur was estimated as BaSO_4 .

The molecular weight of the complexes was determined cryoscopically in freezing nitrobenzene using a Beckmann thermometer of accuracy of ± 0.01 °C in the laboratory. The conductivity measurements were carried out using a Toshniwal Conductivity Bridge (type CL 01/01) and a dip type cell operated at 220 volts AC mains. All the measurements were done at room temperature in PhNO_2 . The magnetic measurements were carried out at room temperature with Evans magnetic balance and anhydrous copper sulfate was used as a calibrant. The infrared spectra of the complexes were recorded on a Perkin Elmer infrared spectrophotometer model 521 in CsI in the range of 4000-200 cm^{-1} . A Hilger Unispeak spectrophotometer with 1 cm quartz cell was employed for recording the visible spectra of Pr^{3+} , Na^{3+} , and Sm^{3+} complexes. Thermogravimetric analysis of these coordination compounds was carried out in static air, with open sample holder and small platinum boat, the heating rate was 6°min^{-1} .

RESULTS AND DISCUSSION

The reaction of non-aqueous solutions of lanthanide(III) salts with CAAPS as primary ligand and DPSO as secondary

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ligand resulting complexes of the general composition $\text{LnX}_{3,n}(\text{CAAPS})\cdot\text{DPSO}$ ($\text{X} = \text{NCS}$ or ClO_4 , $n = 2$, $\text{X} = \text{NO}_3$, $n = 1$). The complexes are anhydrous in nature, which is evident from their analytical, infrared and thermal studies. All the complexes are quite stable and can be stored for long period. The complexes are generally soluble in common organic solvents but insoluble in diethyl ether. All the complexes are also soluble in weak coordinating solvents such as DMSO or DMF. The analytical data presented in Table 1 indicates that the complexes are pure and need no further purification.

TG curves indicate no changes up to, 130 °C suggesting the absence of either coordinated or uncoordinating water molecule in these complexes. The molar conductance of nitrate and thiocyanato complexes in nitrobenzene are too low to account for any dissociation, therefore, the complexes are non-electrolyses. The perchlorato complexes behave as 1:3 electrolytes in nitrobenzene.

Data on the molecular weight of these complexes in nitrobenzene are also presented in Table 1 along with the values calculated on the basis of established formula of the complexes. The ratio of molecular weight observed for $\text{Ln}(\text{NO}_3)_3\cdot(\text{CAAPS})\cdot\text{DPSO}$ or $\text{Ln}(\text{NCS})_3\cdot 2(\text{CAAPS})\cdot\text{DPSO}$ to that calculated is ~0.98 which shows that the complexes are monomeric in solution. In the case of $\text{Ln}(\text{ClO}_4)_3\cdot(\text{CAAPS})\cdot\text{DPSO}$ the ratio is found to be 0.25. The data further support that four species are formed in the perchlorato complexes.

The magnetic moment values observed in these

coordination compounds are presented in Table 1 show that the lanthanum complexes are diamagnetic in nature, as expected from its closed shell electronic configuration and absence of unpaired electrons. All other tripositive, lanthanide ions are paramagnetic due to the presence of 4*f*-electrons, which are effectively shielded by $5s^25p^6$ electrons.

The comparison of these observed values with those observed for $\text{Ln}_2(\text{SO}_4)_3\cdot 8\text{H}_2\text{O}$ [9] and those calculated for uncomplexed ions [10], indicated that the 4*f*-electrons do not participate in any bond formation in these complexes. The compounds discussed herein show a little deviation from the Van Vleck values [11] although the simple Curie equation has been used. This was to be expected as the crystal field splitting of the *f*-orbitals was of the order of 100 cm^{-1} , a value quite inadequate to bring about electron pairing or even an altered magnetic moment due to thermal population of excited states whose degenerate levels have been split by the crystal field. It was just possible that the splitting of the lowest excited state of $\text{Sm}(^6\text{H}_{7/2})$ might have given an altered value of the magnetic moment, but this effect was not observed. Thus the magnetic moments of the new complexes reported herein are within the range predicted and observed in the compounds of paramagnetic ions as reported earlier [12-14].

Infrared Spectra

The key infrared bands of these complexes are given in Table 2. In the present complexes, as expected the $\nu(\text{NH}_2)$ of the hydrazinic nitrogen of semicarbazide ($\sim 1622\text{ cm}^{-1}$) is

Table 1. Analytical, Conductivity, Molecular Weight and Magnetic Susceptibility Data of Lanthanide(III) Complexes of CAAPS and DPSO

Compound	%Analysis, Found (Calcd.)				m.w. found (Calcd.)	Λ_m ($\text{ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$)	μ_{eff} (B.M.)
	Ln	N	S	Anion			
$\text{La}(\text{NO}_3)_3\cdot(\text{CAAPS})\cdot\text{DPSO}$	15.32 (15.42)	13.87 (13.98)	3.51 (3.55)	-	897 (901)	1.9	Diamag.
$\text{Pr}(\text{NO}_3)_3\cdot(\text{CAAPS})\cdot\text{DPSO}$	15.50 (15.61)	13.84 (13.95)	3.50 (3.54)	-	899 (903)	2.1	3.60
$\text{Nd}(\text{NO}_3)_3\cdot(\text{CAAPS})\cdot\text{DPSO}$	15.78 (15.89)	13.79 (13.90)	3.49 (3.53)	-	903 (906)	1.7	3.57
$\text{Sm}(\text{NO}_3)_3\cdot(\text{CAAPS})\cdot\text{DPSO}$	16.34 (16.44)	13.70 (13.81)	3.45 (3.50)	-	907 (912)	2.2	1.71

Table 1. Continued

Gd(NO ₃) ₃ ·(CAAPS)·DPSO	16.96 (17.08)	13.59 (13.71)	3.44 (3.48)	-	915 (919)	1.8	7.84
Tb(NO ₃) ₃ ·(CAAPS)·DPSO	17.15 (17.26)	13.58 (13.68)	3.43 (3.47)	-	916 (921)	1.7	9.38
Dy(NO ₃) ₃ ·(CAAPS)·DPSO	17.47 (17.57)	13.52 (13.62)	3.42 (3.46)	-	919 (924.5)	1.8	10.58
Ho(NO ₃) ₃ ·(CAAPS)·DPSO	17.70 (17.81)	13.50 (13.60)	3.41 (3.45)	-	922 (926)	2.0	10.30
La(NCS) ₃ ·2(CAAPS)·DPSO	10.91 (11.00)	16.52 (16.62)	10.05 (10.13)	13.66 (13.77)	1258 (1263)	2.3	Diamag.
Pr(NCS) ₃ ·2(CAAPS)·DPSO	11.05 (11.14)	16.50 (16.60)	10.02 (10.11)	13.65 (13.75)	1260 (1265)	2.1	3.58
Nd(NCS) ₃ ·2(CAAPS)·DPSO	11.26 (11.35)	16.46 (16.56)	10.00 (10.09)	13.62 (13.72)	1263 (1268)	2.2	3.60
Sm(NCS) ₃ ·2(CAAPS)·DPSO	11.68 (1.77)	16.38 (16.48)	9.99 (10.04)	13.55 (13.65)	1269 (1274)	1.9	1.68
Gd(NCS) ₃ ·2(CAAPS)·DPSO	12.17 (12.25)	16.28 (16.39)	9.94 (9.99)	13.48 (13.58)	1276 (1281)	2.2	7.89
Tb(NCS) ₃ ·2(CAAPS)·DPSO	12.30 (12.39)	16.25 (16.36)	9.93 (9.97)	13.46 (13.56)	1278 (1283)	1.8	9.72
Dy(NCS) ₃ ·2(CAAPS)·DPSO	12.53 (12.63)	16.21 (16.32)	9.89 (9.94)	13.43 (13.52)	1282 (1286.5)	2.3	10.51
Ho(NCS) ₃ ·2(CAAPS)·DPSO	12.68 (12.80)	16.18 (16.29)	9.88 (9.93)	13.39 (13.49)	1284 (1289)	2.1	10.43
La(ClO ₄) ₃ ·2(CAAPS)·DPSO	9.92 (10.01)	11.99 (12.10)	2.26 (2.30)	21.40 (21.51)	346 (1347.5)	78.2	Diamag.
Pr(ClO ₄) ₃ ·2(CAAPS)·DPSO	10.06 (10.14)	11.98 (12.09)	2.26 (2.30)	21.37 (21.48)	347 (1389.5)	76.9	3.67
Nd(ClO ₄) ₃ ·2(CAAPS)·DPSO	10.25 (10.34)	11.94 (12.06)	2.25 (2.29)	21.32 (21.43)	349 (1392.5)	79.2	3.58
Sm(ClO ₄) ₃ ·2(CAAPS)·DPSO	10.63 (10.72)	11.90 (12.01)	2.24 (2.28)	21.22 (21.34)	350 (1398.5)	77.7	1.64
Gd(ClO ₄) ₃ ·2(CAAPS)·DPSO	11.07 (11.17)	11.84 (11.95)	2.23 (2.27)	21.13 (21.23)	351 (1405.5)	78.7	7.89
Tb(ClO ₄) ₃ ·2(CAAPS)·DPSO	11.19 (11.29)	11.82 (11.93)	2.23 (2.27)	21.09 (21.20)	352 (1407.5)	78.3	9.28
Dy(ClO ₄) ₃ ·2(CAAPS)·DPSO	11.40 (11.51)	11.79 (11.90)	2.22 (2.26)	21.04 (21.15)	352 (1411)	78.9	10.53
Ho(ClO ₄) ₃ ·2(CAAPS)·DPSO	11.56 (11.67)	11.79 (11.88)	2.22 (2.26)	21.00 (21.11)	353 (1413.5)	77.8	10.29

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Table 2. Key Infrared Spectral Bands (cm^{-1}) of Mixed Ligand Complexes of Lanthanides(III) with CAAPS and DPSO

Compounds	$\nu(\text{S}=\text{O})$	$\nu(\text{C}=\text{N})$ Azomethinic	$\nu(\text{C}=\text{N})$ Hydrazinic	$\nu(\text{C}=\text{O})$			$\nu(\text{Ln}-\text{O})/$ $\nu(\text{Ln}-\text{N})$
				I	II	III	
				DPSO	1030vs	-	
CAAPS	-	1610m	1600m	1700m	1572m	1350m	-
La(NO ₃) ₃ .(CAAPS).DPSO	950s	1580m	1630m	1650m	1540m	1330m	460m, 395w
Pr(NO ₃) ₃ .(CAAPS).DPSO	952s	1585m	1632m	1652m	1535m	1325m	462m, 390w
Nd(NO ₃) ₃ .(CAAPS).DPSO	945s	1582m	1628m	1655m	1538m	1332m	455m, 385w
Sm(NO ₃) ₃ .(CAAPS).DPSO	950s	1580m	1625m	1650m	1535m	1320m	470m, 399w
Gd(NO ₃) ₃ .(CAAPS).DPSO	955s	1587m	1630m	1652m	1540m	1325m	475m, 398w
Tb(NO ₃) ₃ .(CAAPS).DPSO	952s	1585m	1632m	1648m	1537m	1322m	468m, 395w
Dy(NO ₃) ₃ .(CAAPS).DPSO	965s	1580m	1630m	1645m	1535m	1320m	458m, 392w
Ho(NO ₃) ₃ .(CAAPS).DPSO	960s	1582m	1625m	1650m	1536m	1325m	462m, 392w
La(NCS) ₃ .2(CAAPS).DPSO	955s	1578m	1630m	1652m	1542m	1323m	465m, 396w
Pr(NCS) ₃ .2(CAAPS).DPSO	955s	1580m	1632m	1648m	1540m	1320m	468m, 395w
Nd(NCS) ₃ .2(CAAPS).DPSO	950s	1578m	1630m	1646m	1542m	1322m	465m, 398w
Sm(NCS) ₃ .2(CAAPS).DPSO	952s	1575m	1630m	1645m	1540m	1320m	460m, 395w
Gd(NCS) ₃ .2(CAAPS).DPSO	955s	1582m	1630m	1650m	1538m	1322m	472m, 398w
Tb(NCS) ₃ .2(CAAPS).DPSO	958s	1580m	1628m	1645m	1537m	1325m	475m, 390w
Dy(NCS) ₃ .2(CAAPS).DPSO	962s	1575m	1625m	1650m	1540m	1330m	468m, 392w
Ho(NCS) ₃ .2(CAAPS).DPSO	960s	1580m	1628m	1642m	1538m	1328m	470m, 395w
La(ClO ₄) ₃ .2(CAAPS).DPSO	950s	1582m	1630m	1645m	1535m	1325m	458m, 387w
Pr(ClO ₄) ₃ .2(CAAPS).DPSO	948s	1578m	1632m	1642m	1540m	1328m	462m, 390w
Nd(ClO ₄) ₃ .2(CAAPS).DPSO	945s	1580m	1630m	1645m	1542m	1330m	465m, 392w
Sm(ClO ₄) ₃ .2(CAAPS).DPSO	948s	1582m	1632m	1650m	1540m	1332m	460m, 390w
Gd(ClO ₄) ₃ .2(CAAPS).DPSO	950s	1580m	1630m	1645m	1540m	1320m	462m, 395w
Tb(ClO ₄) ₃ .2(CAAPS).DPSO	948s	1578m	1632m	1648m	1542m	1322m	465m, 398w
Dy(ClO ₄) ₃ .2(CAAPS).DPSO	950s	1585m	1632m	1645m	1538m	1325m	460m, 395w
Ho(ClO ₄) ₃ .2(CAAPS).DPSO	948s	1580m	1630m	1645m	1536m	1326m	472m, 390w

absent in the infrared spectra [8]. It has also been observed that the amide-II band is shifted towards the lower energy side compared to that of the semicarbazone. The effect is due to the electron density drift from the hydrazinic nitrogen [15,16]. The characteristic absorption of the carbonyl group in CAAPS is observed at $\sim 1700 \text{ cm}^{-1}$ [17,18]. In the complexes, this band is shifted toward lower energy in $1650\text{-}1640 \text{ cm}^{-1}$ region (Table 3). The amide-II band in free ligand (CAAPS) has been observed at 1560 cm^{-1} . In all the present complexes this band is also shifted towards lower wave numbers by ~ 30

cm^{-1} . This observation suggests coordination through the carbonyl-oxygen atom. The strong band at $\sim 1605 \text{ cm}^{-1}$ in CAAPS apparently has a large contribution from the $\nu(\text{C}=\text{N})$ band in all the complexes as compared to the free ligand. Another strong band was observed at 1620 cm^{-1} due to azomthine ($\text{C}=\text{N}$) absorption. On complexation, this band is shifted towards the lower frequency region, clearly indicating the coordination through the azomethine N-atom [19-21]. In far infrared region the bands due to $\nu(\text{Ln}-\text{N})/\nu(\text{Ln}-\text{O})$ are also observed [22-25].

Table 3. Infrared Absorption Frequency (cm^{-1}) of NO_3^- Ion in $\text{Ln}(\text{NO}_3)_3 \cdot (\text{CAAPS}) \cdot \text{DPSO}$

Complex	$(\nu_2 + \nu_5)$	$(\nu_2 + \nu_6)$	$(\nu_2 + \nu_5) -$ $(\nu_2 + \nu_6)$	ν_4	ν_1	ν_2	ν_6	ν_3	ν_5
$\text{La}(\text{NO}_3)_3 \cdot (\text{CAAPS}) \cdot \text{DPSO}$	1780vw	1728vw	52	1505s	1290m	1025m	820m	737m	690w
$\text{Pr}(\text{NO}_3)_3 \cdot (\text{CAAPS}) \cdot \text{DPSO}$	1785vw	1735vw	50	1510s,br	1285m	1022m	825m	742m	700w
$\text{Nd}(\text{NO}_3)_3 \cdot (\text{CAAPS}) \cdot \text{DPSO}$	1780vw	1740vw	40	1510sh, 1485s,br	1290s	1032m	822m	740m	698w
$\text{Sm}(\text{NO}_3)_3 \cdot (\text{CAAPS}) \cdot \text{DPSO}$	1778vw	1740vw	38	1515m	1292s	1025m	810m	725m	-
$\text{Gd}(\text{NO}_3)_3 \cdot (\text{CAAPS}) \cdot \text{DPSO}$	1785vw	1740vw	45	1505sh 1500m	1305s	1030m	822s	730m	695w
$\text{Tb}(\text{NO}_3)_3 \cdot (\text{CAAPS}) \cdot \text{DPSO}$	1778vw	1735vw	43	1498s,br	1285m	1028m	815s	735m	700m
$\text{Dy}(\text{NO}_3)_3 \cdot (\text{CAAPS}) \cdot \text{DPSO}$	1790vw	1745vw	45	1500s	1290m	1025m	822s	730m	702w
$\text{Ho}(\text{NO}_3)_3 \cdot (\text{CAAPS}) \cdot \text{DPSO}$	1785vw	1730vw	55	1495s,br	1285m	1032m	828m	728m	690sh

Sulfoxides act as an electron pair donor forming molecular adducts or complexes with a variety of acceptor molecules. Sulfoxides contain a soft sulfur and a hard oxygen, both of which can act as nucleophiles. Although both oxygen and sulfur coordinated sulfoxide complexes are known with transition and non-transition metal ions [26,27], only oxygen coordinated sulfoxide coordination compounds are formed with the lanthanide metal ions [5]. In the infrared spectra of free DPSO, the (S=O) stretching vibration [26-28] appears as a strong band at 1030 cm^{-1} , while in the spectra of its coordination compounds, it is shifted to $960\text{-}950 \text{ cm}^{-1}$ (Table 3). The (C-S) stretching absorption in free DPSO occurs at 680 cm^{-1} , which undergoes a slight positive shift on complexation. A negative shift of the (S=O) stretching frequency and a shift of the (C-S) stretching frequency towards a higher wave numbers are indicative of the decrease in the double bond character of the (S=O) bond and an electron shift from the aryl group to the sulfur atom of the ligand. The data thus suggests coordination from the oxygen atom to the DPSO.

Anion Vibrations

In $\text{Ln}(\text{NO}_3)_3 \cdot (\text{CAAPS}) \cdot \text{DPSO}$ complex, the occurrence of two strong vibrations at $1525\text{-}1515 \text{ cm}^{-1}$ and $1310\text{-}1290 \text{ cm}^{-1}$ region is, attributed to ν_4 and ν_1 modes of vibration of the covalently bonded nitrate groups respectively, suggesting that

the nitrate groups lie inside the coordination spheres [29,30]. Other absorptions associated with the covalent nitrate groups are also observed in the spectra of these complexes. If the $(\nu_4 - \nu_1)$ difference is taken as an approximate measure of the covalency of the nitrate groups [30], a value of $\sim 200 \text{ cm}^{-1}$ for the complexes studied herein suggest strong covalency for the metal-nitrate bonding. Though considerable work has been carried out in order to establish the nature of coordinated nitrate by infrared studies, it is not possible to identify the type of bonding with certainty since the symmetry of the nitrate group remains the same, whether it acts as a monodentate or bidentate group. In some cases, Lever Separation method [31], *i.e.*, the number and relative energies of nitrate combination frequencies in the $1800\text{-}1700 \text{ cm}^{-1}$ region of the infrared spectra, has been used as an aid to distinguish the various coordination modes of nitrate groups. According to Level *et al.* [31] bidentate coordination involves a greater distortion from D_{3h} symmetry than monodentate coordination, therefore, bidentate complexes should show a large separation of $(\nu_1 + \nu_4)$. By an investigation of the spectra of a number of compounds of known crystal structure, Lever *et al.* [31] showed this to be true, the separation for monodentate nitrate groups appeared to be $5\text{-}26 \text{ cm}^{-1}$ and that for bidentate group $25\text{-}66 \text{ cm}^{-1}$. Nevertheless the authors in the present work have tried to apply this method to $[\text{Ln}(\text{NO}_3)_3 \cdot (\text{CAAPS}) \cdot \text{DPSO}]$ complexes (Table 3). The separation of $30\text{-}40 \text{ cm}^{-1}$ in the

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Table 4. Infrared Absorption Frequencies (cm^{-1}) of NCS^- in $\text{Ln}(\text{NCS})_3 \cdot 2(\text{CAAPS}) \cdot \text{DPSO}$

Complex	$\nu(\text{CN})$	$\nu(\text{CS})$	$\delta(\text{NCS})$
$\text{La}(\text{NCS})_3 \cdot 2(\text{CAAPS}) \cdot \text{DPSO}$	2045m	842m	468w
$\text{Pr}(\text{NCS})_3 \cdot 2(\text{CAAPS}) \cdot \text{DPSO}$	2040s	840m	470w
$\text{Nd}(\text{NCS})_3 \cdot 2(\text{CAAPS}) \cdot \text{DPSO}$	2050s	845m	462w
$\text{Sm}(\text{NCS})_3 \cdot 2(\text{CAAPS}) \cdot \text{DPSO}$	2035s	838m	460m
$\text{Gd}(\text{NCS})_3 \cdot 2(\text{CAAPS}) \cdot \text{DPSO}$	2042s	845m	472w
$\text{Tb}(\text{NCS})_3 \cdot 2(\text{CAAPS}) \cdot \text{DPSO}$	2050s	850m	465m
$\text{Dy}(\text{NCS})_3 \cdot 2(\text{CAAPS}) \cdot \text{DPSO}$	2048s	842m	-
$\text{Ho}(\text{NCS})_3 \cdot 2(\text{CAAPS}) \cdot \text{DPSO}$	2045s	835m	470w

combination bands ($\nu_1 + \nu_4$) in the 1800-1700 cm^{-1} region concludes the bidentate nitrate coordination. The bidentate character of nitrate groups has been established by X-ray [32] and neutron diffraction studies [35]. It is infrared which indicates that the nitrate groups in these complexes are of bidentate in nature.

In case of thiocyanate complexes, it is difficult to establish unambiguously from the infrared spectra whether the thiocyanate group is N or S bonded to lanthanide metal ions. According to the “hard” and “soft” concept of Pearson [36], one would expect the NCS^- ion, in which N is hard to coordinate by that atom to hard acids, such as Chatt-Ahrlund class-A metals like lanthanides or actinides, whereas S in the SCN^- is “soft” and should therefore be the atom coordinated to class-B metals. The (C-N) stretching frequency in $[\text{Ln}(\text{NCS})_3 \cdot 2(\text{CAAPS}) \cdot \text{DPSO}]$ appears in 2070-2040 cm^{-1} region which lies on the border line for distinguishing between sulfur and nitrogen bonding in the thiocyanate [37], although the high relative intensity of the band in these cases suggests that the thiocyanate groups are N-bonded [38,39]. The frequency of the (C-S) stretching vibration has also been used to diagnose the bonding mode in thiocyanate [40,41]. The (C-S) bond identified in 840-780 cm^{-1} region further confirms that the thiocyanate group is N-bonded [42-45]. The $\delta(\text{N-C-S})$ (ν_2) is also identified in these complexes (Table 4).

The occurrence of two strong bands at ~1080 and 620 cm^{-1} in the spectra of perchlorate complexes attributed to ν_3 and ν_4 vibrations of the ionic perchlorate suggest [46,47] that the

Table 5. Infrared Absorption Frequencies (cm^{-1}) of ClO_4^- in $\text{Ln}(\text{ClO}_4)_3 \cdot 2(\text{CAAPS}) \cdot \text{DPSO}$

Complex	ν_3	ν_4
$\text{La}(\text{ClO}_4)_3 \cdot 2(\text{CAAPS}) \cdot \text{DPSO}$	1105s	632s
$\text{Pr}(\text{ClO}_4)_3 \cdot 2(\text{CAAPS}) \cdot \text{DPSO}$	1085s	628s
$\text{Nd}(\text{ClO}_4)_3 \cdot 2(\text{CAAPS}) \cdot \text{DPSO}$	1100s	630s
$\text{Sm}(\text{ClO}_4)_3 \cdot 2(\text{CAAPS}) \cdot \text{DPSO}$	1095s	625s
$\text{Gd}(\text{ClO}_4)_3 \cdot 2(\text{CAAPS}) \cdot \text{DPSO}$	1080s	622s
$\text{Tb}(\text{ClO}_4)_3 \cdot 2(\text{CAAPS}) \cdot \text{DPSO}$	1085s	625s
$\text{Dy}(\text{ClO}_4)_3 \cdot 2(\text{CAAPS}) \cdot \text{DPSO}$	1102s	628s
$\text{Ho}(\text{ClO}_4)_3 \cdot 2(\text{CAAPS}) \cdot \text{DPSO}$	1105s	635s

perchlorate group are present outside the coordination sphere [48-50]. In present complexes $[\text{Ln}(\text{CAAPS})_2 \cdot \text{DPSO}](\text{ClO}_4)_3$, the presence of very strong ν_3 band is in 1105-1080 cm^{-1} and strong narrow ν_4 band is 630-620 cm^{-1} region indicate tetrahedral symmetry of the perchlorate ion, which is not bonded to Ln^{3+} ion [49-50] (Table 5).

Electronic Spectra

The electronic spectra of the solutions of the present trivalent lanthanide complexes investigated in CH_3CN are recorded in Table 6-8 and for comparison, data for an aqueous salt solution are also given. Lanthanide(III) has no significant absorption in the visible region. The absorption bands of Pr(III), Nd(III), Sm(III), Gd(III), and Dy(III) in the visible and near infrared region appear due to transitions from the ground levels $^3\text{H}_4$, $^4\text{I}_{9/2}$, $^6\text{H}_{5/2}$, $^8\text{S}_{7/2}$, and $^6\text{H}_{15/2}$ to the excited J-levels of 4f-configuration, respectively. Some red shift or nephelauxetic effect is observed in CH_3CN solution of these coordination compounds. This red shift is usually accepted as an evidence of a higher degree of covalency than existing in the aquo compounds [51,52]. In all the complexes a marked enhancement in the intensity of the band has been observed. This red shift of the hypersensitive bands has been utilized to calculate the nephelauxetic effect (β) in these chelate complexes. From the β -values, the covalence factors ($b^{1/2}$), Sinha parameter ($\delta\%$) (metal-ligand, covalency, per cent) and the covalency angular overlap parameter (η) have been calculated using the following expression [52,53].

Table 6. Electronic Spectral Data (cm⁻¹) and Related Bonding Parameters of Mixed Ligand Complexes of Lanthanide(III) Nitrate with CAAPS and DPSO

Complex	Ln(NO ₃) ₃ spectral bands	Complex electronic spectral bands	Energy levels	(1- β)	β	b ^{1/2}	δ%	η
Pr(NO ₃) ₃ .(CAAPS).DPSO	22470	22300	³ H ₄ → ³ P ₂	0.0075	0.9925	0.0433	0.7556	0.0038
	21280	21120	→ ³ P ₁	0.0075	0.9925	0.0433	0.7556	0.0038
	20830	20680	→ ³ P ₀	0.0072	0.9928	0.0424	0.7252	0.0036
	16950	16780	→ ¹ D ₂	0.0100	0.9900	0.0500	1.0100	0.0050
Nd(NO ₃) ₃ .(CAAPS).DPSO	19420	19260	⁴ I _{9/2} → ² G _{9/2}	0.0082	0.9918	0.0452	0.8267	0.0042
	17390	17220	→ ⁴ G _{5/2} , ² G _{7/2}	0.0097	0.9903	0.0049	0.9795	0.0049
	13420	13220	→ ² S _{3/2} , ⁴ F _{7/2}	0.0149	0.9851	0.0610	1.5125	0.0075
	12500	12320	→ ⁴ F _{5/2} , ⁴ H _{9/2}	0.0144	0.9856	0.0600	1.4610	0.0073
Sm(NO ₃) ₃ .(CAAPS).DPSO	24850	24700	⁴ H _{9/2} → ⁴ F _{9/2}	0.0060	0.9940	0.0387	0.6036	0.0031
	24100	23890	→ ⁶ P _{5/2}	0.0087	0.9913	0.0466	0.8776	0.0044
	21600	21480	→ ⁴ I _{13/2}	0.0055	0.9945	0.0370	0.5530	0.0028

Table 7. Electronic Spectral Data (cm⁻¹) and Related Bonding Parameters of Mixed Ligand Complexes of Lanthanide(III) Isothiocyanate with CAAPS and DPSO

Complex	Ln(NO ₃) ₃ spectral bands	Complex electronic spectral bands	Energy levels	(1- β)	β	b ^{1/2}	δ%	η
Pr(NCS) ₃ .2(CAAPS).DPSO	22,400	22,220	³ H ₄ → ³ P ₂	0.0080	0.9920	0.0447	0.8064	0.0040
	21,230	21,080	→ ³ P ₁	0.0070	0.9930	0.0418	0.7049	0.0035
	20,800	20,650	→ ³ P ₀	0.0072	0.9928	0.0424	0.7252	0.0036
	16,900	16,750	→ ¹ D ₂	0.0088	0.9912	0.0469	0.8878	0.0044
Nd(NCS) ₃ .2(CAAPS).DPSO	19,300	19,150	⁴ I _{9/2} → ² G _{9/2}	0.0077	0.9923	0.0438	0.7760	0.0039
	17,400	17,250	→ ⁴ G _{5/2} , ² G _{7/2}	0.0086	0.9914	0.0463	0.8674	0.0043
	13,400	13,230	→ ² S _{3/2} , ⁴ F _{7/2}	0.0126	0.9874	0.0561	1.2760	0.0064
	12,500	12,320	→ ⁴ F _{5/2} , ⁴ H _{9/2}	0.0144	0.9856	0.0600	1.4610	0.0073
Sm(NCS) ₃ .2(CAAPS).DPSO	24900	24,750	⁴ H _{9/2} → ⁴ F _{9/2}	0.0060	0.9940	0.0387	0.6036	0.0033
	24000	23,850	→ ⁶ P _{5/2}	0.0062	0.9938	0.0393	0.6238	0.0032
	21600	21,450	→ ⁴ I _{13/2}	0.0069	0.9930	0.0415	0.6948	0.0035

Seven and Ten Coordinated Complexes of Trivalent Lanthanides

Table 8. Electronic Spectral Data (cm⁻¹) and Related Bonding Parameters of Mixed Ligand Complexes of Lanthanide(III) Perchlorate with CAAPS and DPSO

Complex	Ln(ClO ₄) ₃ spectral bands	Complex electronic spectral bands	Energy levels	(1 - β)	β	b ^{1/2}	δ%	η
Pr(ClO ₄) ₃ .2(CAAPS).DPSO	22,470	22,350	³ H ₄ → ³ P ₂	0.0053	0.9946	0.0364	0.5328	0.0027
	21,325	21,180	→ ³ P ₁	0.0068	0.9932	0.0412	0.6846	0.0035
	20,750	20,600	→ ³ P ₀	0.0072	0.9928	0.0424	0.7252	0.0036
	17,000	16,840	→ ¹ D ₂	0.0094	0.9906	0.0484	0.9489	0.0047
Nd(ClO ₄) ₃ .2(CAAPS).DPSO	19,600	19,480	⁴ I _{9/2} → ² G _{9/2}	0.0061	0.9939	0.0390	0.6137	0.0030
	17,380	17,200	→ ⁴ G _{5/2} , ² G _{7/2}	0.0103	0.9897	0.0507	1.0407	0.0584
	13,680	13,500	→ ² S _{3/2} , ⁴ F _{7/2}	0.0131	0.9869	0.0572	1.3273	0.0066
	12,470	12,300	→ ⁴ F _{5/2} , ⁴ H _{9/2}	0.0136	0.9864	0.0583	1.3787	0.0069
Sm(ClO ₄) ₃ .2(CAAPS).DPSO	24,870	24,750	⁶ H _{5/2} → ⁴ F _{9/2}	0.0048	0.9952	0.0346	0.4823	0.0025
	24,000	23,820	→ ⁶ P _{5/2}	0.0075	0.9925	0.0433	0.7556	0.0038
	21,550	21,400	→ ⁴ I _{13/2}	0.0069	0.9931	0.0415	0.6948	0.0035

$$b^{1/2} = \frac{1}{2}[(1 - \beta)^{1/2}]$$

$$(\delta\%) = [(1 - \beta)/\beta] \times 100$$

$$\eta = (1 - \beta)^{1/2}/\beta^{1/2}$$

The positive values of (1 - β) and δ% in these coordination compounds (Table 7-9) suggest that the bonding between metal and the ligand is covalent as compared with the bonding between the metal and an aquo ligand. The values of covalence factor (b^{1/2}) and angular overlap parameter (η) were found to be positive indicating covalent bonding.

Thermogravimetric Studies

(i) **Ln(NO₃)₃.(CAAPS).DPSO (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho).** Thermoanalytical results of these complexes are presented in Table 9. The pyrolysis curves of these complexes indicate virtually no change in weight up to 115 °C. At 115-160 °C, a loss of 22.38-22.89% has been observed, which corresponds to the evaporation of one DPSO ligand. Further a loss of 62.70-64.26% in 235-375 °C temperature region showing the loss of CAAPS ligand. The lanthanide oxide (Pr₆O₁₁, Nd₂O₃, Sm₂O₃ or Ho₂O₃) is the final

product at ~830 °C [54-56].

(ii) **Ln(NCS)₃.2(CAAPS).DPSO (Ln = La, Sm or Dy).**

Thermoanalytical results of these complexes are presented in Table 10. The pyrolysis curves of these complexes in 120-160 °C, show a loss in weight (16.20-16.45%) which corresponds to the evaporation of one DPSO ligand. After that there is no virtual changes in these curves upto 220 °C. In temperature region 220-240 °C, the complexes started to loss mass with partial evaporation of CAAPS, the loss of mass (45.50-46.20 %) corresponds to one mole of CAAPS. At 290 °C, the remaining CAAPS is also lost. The residue obtained after heating at ~840 °C to constant weight, is very closed to that expected for lanthanide oxides [54-56].

(iii) **Ln(ClO₄)₃.2(CAAPS).DPSO (Ln = Pr, Sm or Gd).**

The pyrolysis curve of [Ln(CAAPS)₂.DPSO].(ClO₄)₃ (Ln = Pr, Sm or Gd) indicate that the complexes do not possess water of crystallization. The complexes are stable up to 125 °C, beyond which they started to lose mass up to a temperature of 160 °C corresponding to loss of one molecule of DPSO. Further analysis of thermal curves reveals that the complexes lose mass with partial evaporation of CAAPS up to 225 °C. The mass loss corresponds to one molecule of CAAPS. In the temperature range 240-285 °C, another molecule of CAAPS is

Table 9. Thermoanalytical Results of Some Mixed Ligand Complexes of Lanthanide(III) Nitrate with CAAPS and DPSO

Complex	Sample wt (mg)	Residual wt (mg)	Ligand mass loss (%)				Residual (%)	
			120-160 °C		260-350 °C		~825 °C	
			Theor. ^a	Exp.	Theor. ^b	Exp.	Theor. ^b	Exp.
Pr(NO ₃) ₃ .(CAAPS).DPSO	13.20	2.45	22.36	22.89	63.78	64.26	18.86	18.59
Nd(NO ₃) ₃ .(CAAPS).DPSO	14.60	2.68	22.29	22.72	63.57	64.24	18.54	18.39
Sm(NO ₃) ₃ .(CAAPS).DPSO	16.80	3.15	22.15	21.60	63.15	63.76	19.07	18.78
Ho(NO ₃) ₃ .(CAAPS).DPSO	19.20	3.80	21.79	22.38	62.13	62.70	20.38	19.86

^aCalculated for loss of DPSO. ^bCalculated for loss of CAAPS. ^cCalculated for lanthanide oxides (Pr₆O₁₁, Nd₂O₃, Sm₂O₃, Ho₂O₃).

Table 10. Thermoanalytical Results of Some Mixed Ligand Complexes of Lanthanide(III) Isothiocyanate with CAAPS and DPSO

Complex	Sample wt (mg)	Residual wt (mg)	Ligand mass loss (%)						Residual (%)	
			120-160 °C		210-250 °C		280-325 °C		~840 °C	
			Theor. ^a	Exp.	Theor. ^b	Exp.	Theor. ^c	Exp.	Theor. ^d	Exp.
La(NCS) ₃ .2(CAAPS).DPSO	12.60	1.60	15.99	16.45	45.60	46.20	75.21	75.90	12.90	12.74
Sm(NCS) ₃ .2(CAAPS).DPSO	14.20	1.90	15.85	16.38	45.21	45.86	74.56	75.26	13.65	13.40
Dy(NCS) ₃ .2(CAAPS).DPSO	16.40	2.34	15.70	16.20	44.77	45.50	73.84	74.48	14.49	14.27

^aCalculated for loss of DPSO. ^bCalculated for loss of one mole of CAAPS. ^cCalculated for total loss of CAAPS. ^dCalculated for lanthanide oxides (La₂O₃, Sm₂O₃, Dy₂O₃).

Table 11. Thermoanalytical Results of Some Mixed Ligand Complexes of Lanthanide(III) Perchlorate with CAAPS and DPSO

Complex	Sample wt (mg)	Residual wt (mg)	Ligand mass loss (%)				Residual (%)			
			125-160 °C		195-225 °C		240-285 °C		~825 °C	
			Theor. ^a	Exp.	Theor. ^b	Exp.	Theor. ^c	Exp.	Theor. ^d	Exp.
Pr(ClO ₄) ₃ .2(CAAPS).DPSO	12.60	1.52	14.53	14.88	41.45	41.90	68.36	68.98	12.25	12.14
Sm(ClO ₄) ₃ .2(CAAPS).DPSO	14.20	1.74	14.44	14.72	41.18	41.60	67.92	68.42	12.44	12.24
Gd(ClO ₄) ₃ .2(CAAPS).DPSO	16.10	2.02	14.37	14.63	40.98	41.50	67.59	68.24	12.87	12.59

^aCalculated for loss of DPSO. ^bCalculated for loss of one mole of CAAPS. ^cCalculated for total loss of CAAPS. ^dCalculated for lanthanide oxides, (Pr₆O₁₁, Sm₂O₃, Gd₂O₃).

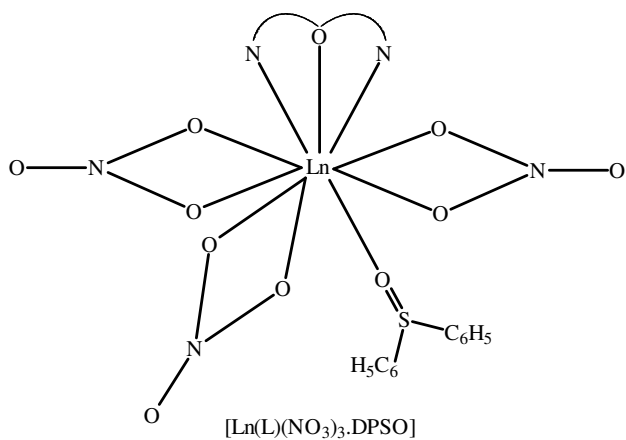
also lost. The residues obtained after heating up to ~825 °C to constant weight is very close to that expected for the lanthanide oxides (Table 11) [54-56].

Stereochemistry

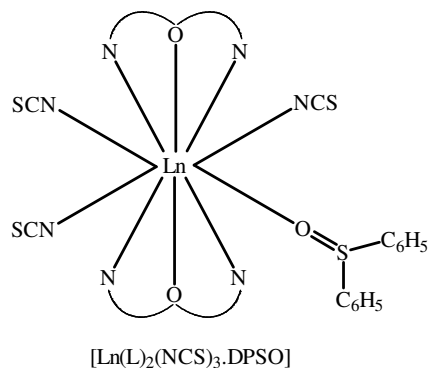
(i) [Ln(CAAPS).DPSO (NO₃)₃] (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho). The conductance measurement of these

coordination compounds in nitrobenzene indicates the nonionic nature of these species. Hence all the three nitrate groups are present inside the coordination sphere. Infrared data reveals the bidentate (O,O) nature of NO₃⁻ group. CAAPS is acting as neutral tridentate (N,N,O-donor) and DPSO is coordinating *via* its lone oxygen atom. Thus lanthanide ions are surrounded by eight oxygen atoms (6-oxygens of three

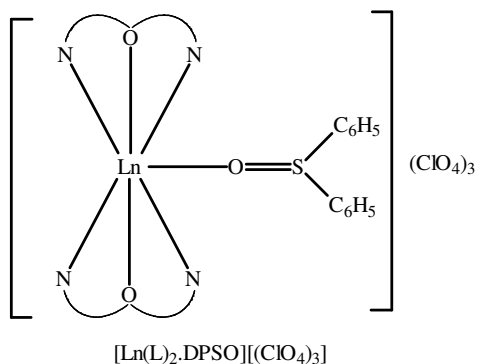
Seven and Ten Coordinated Complexes of Trivalent Lanthanides



(a)



(b)



(c)

Fig. 1. Proposed structures of Lanthanide(III) complexes of HNA-APS and DAAPS.

bidentate nitrate ions, 1-oxygen from amide group of CAAPS and 1-oxygen of DPSO) and 2-nitrogen atoms of azomethine groups of CAAPS and thus produces a coordination number of ten for the central lanthanide ion (Fig. 1a).

(ii) **[Ln(CAAPS)₂.DPSO(NCS)₃]** (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho). The non-electrolytic behaviour of the coordination compounds suggests that all the NCS⁻ ions are coordinated to the central metal ion. Infrared data suggest that the isothiocyanate ions are coordinated to lanthanide ions *via* its N-atom. Since CAAPS is a neutral tridentate (N,N,O) and DPSO is oxygen donor and thus a coordination number ten to the lanthanide ion has been suggested in all these coordination compounds (Fig. 1b).

(iii) **[Ln(CAAPS)₂.DPSO](ClO₄)₃** (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho). The molar conductances of these coordination compounds behave as 1:3 electrolytes. Hence all the three perchlorate ions are not bonded to the lanthanides and present outside the coordination sphere. It is further confirmed by the infrared data. Infrared spectra of all these coordination number seven to lanthanide ion has been assigned in these coordination compounds (Fig. 1c).

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