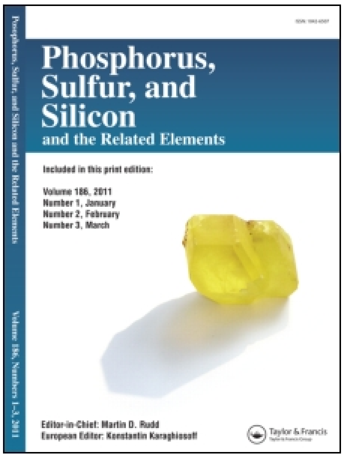

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Studies on the Effect of Various Anions and Pyridine on the Stereochemistry of Lanthanide(III) Coordination Compounds of 4[N-(2'-Hydroxy-1'-Naphthalidene)Amino] Antipyrine Thiosemicarbazone

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To cite this Article Agarwal, Ram K. and Kumar, Vinesh(2010) 'Studies on the Effect of Various Anions and Pyridine on the Stereochemistry of Lanthanide(III) Coordination Compounds of 4[N-(2'-Hydroxy-1'-Naphthalidene)Amino] Antipyrine Thiosemicarbazone', Phosphorus, Sulfur, and Silicon and the Related Elements, 185: 7, 1469 — 1483
To link to this Article: DOI: 10.1080/10426500903085201
URL: http://dx.doi.org/10.1080/10426500903085201

Phosphorus, Sulfur, and Silicon, 185:1469–1483, 2010
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500903085201

STUDIES ON THE EFFECT OF VARIOUS ANIONS AND PYRIDINE ON THE STEREOCHEMISTRY OF LANTHANIDE(III) COORDINATION COMPOUNDS OF 4[N-(2′-HYDROXY-1′-NAPHTHALIDENE)AMINO] ANTIPYRINE THIOSEMICARBAZONE

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In the present studies, the effect of pyridine on stereochemistry of the coordination compounds of lanthanide(III) derived from 4[N-(2′-hydroxy-1′-naphthalidene)amino] antipyrine thiosemicarbazone (HNAAPTS) has been studied. The general composition of the present complexes is $LnX_3 \cdot n(HNAAPTS) \cdot Py$ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho; X = NO_3, n = 1, x = Cl, NCS or ClO_4, n = 2, Py = pyridine). All the complexes were characterized by elemental analyses, molecular weight, molar conductance, magnetic susceptibilities, infrared and electronic spectral studies. The infrared studies reveal that the HNAAPTS behaves as a neutral tridentate (N, N, S), while pyridine is coordinated to metal ions via its nitrogen atom. Nitrates are bicovalently bonded, while thiocyanate is coordinated through a strong N-atom. Perchlorate ions are not coordinating in coordination sphere. From electronic spectral data, nephelauxetic effect (β), covalence factor ($b^{\frac{1}{2}}$), Sinha parameter ($\delta\%$), and the covalence angular overlap parameter (η) have been calculated. Thermal stabilities of these complexes were studied by thermogravimetric analysis. In conclusion, the coordination number of lanthanides(III) in the present compounds is either seven or ten depending on the coordinating anions.

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Keywords Coordination compounds; lanthanide(III); pyridine; stereochemistry; thiosemicarbazone

INTRODUCTION

The introduction of the nitrogen and sulfur atoms into the structure of organic compounds often has important consequences in their behavior towards metal ions. From the comparatively large atomic radius of sulfur atom and its lower electronegativity than nitrogen, one expects that sulfur-containing ligands will form less stable complexes than those containing nitrogen, but it has been observed that the affinity of sulfur for metal ions is often

Received 6 April 2009; accepted 29 May 2009.

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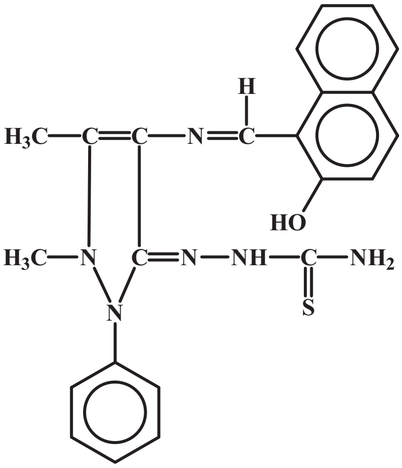

Figure 1 4[N-(2′-Hydroxy-1′-naphthalidene)amino]antipyrine thiosemicarbazone (HNAAPTS) (m.f. $C_{23}H_{22}N_6OS$).

very close to the ligands containing nitrogen as donor atoms. Thiosemicarbazones are not well established as an important class of sulfur donor ligands.[1–3] The interest in developing the coordination chemistry of thiosemicarbazones is due to their biological and medicinal properties. They present a variety of biological activities ranging from antitumor to fungicide, bactericide, anti-inflammatory, and antiviral activities. From our laboratory, we have published oxovanadium(IV), copper(II), UO_2(VI), Co(II), Ni, and Pt-metals complexes of thiosemicarbazones.[4–7] Although a number of trivalent lanthanide(III) complexes of semicarbazones have been reported,[8] less is known about the trivalent lanthanide(III) complexes of thiosemicarbazones.[9,10] In continuation of our work on 4-amino antipyrine–derived thiosemicarbazones complexes of metal ions, this article reports the effect of pyridine on stereochemistry of the coordination compounds of lanthanide(III) derived from 4[N-(2′-hydroxy-1′-naphthalidene)amino]antipyrine thiosemicarbazone (HNAAPTS) (Figure 1).

RESULTS AND DISCUSSION

The interaction of non-aqueous solutions of lanthanide(III) salts with HNAAPTS in the presence of pyridine produces complexes of the general composition $LnX_3 \cdot n(HNAAPTS) \cdot Py$ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho; X = NO_3, n = 1, X = Cl, NCS or ClO_4, n = 2, Py = pyridine). The analytical data of these complexes are presented in Tables I–IV. All the complexes are quite stable and could be stored for months without any appreciable change. The complexes do not have sharp melting points, but decomposed upon heating beyond 260°C. The complexes are generally soluble in common organic solvents. The molar conductance values of these compounds in nitrobenzene are presented in Tables I–IV. The molar conductance values of chloro, thiocyanato, and nitrato complexes are too low to account for any dissociation; thus these complexes are considered to be non-electrolytes. The perchlorato complexes behave as 1:3 electrolytes in nitrobenzene.[15] Data on the molecular weight of the complexes in nitrobenzene are given in Tables I–IV along with values on the basis of established formulae of the complexes. The ratio of molecular weight observed for $LnCl_3 \cdot 2(HNAAPTS) \cdot Py$, $Ln(NCS)_3 \cdot 2(HNAAPTS) \cdot Py$, and

Table I Analytical, conductivity, molecular weight, and magnetic susceptibility of $Ln(NO_3)_3 \cdot (HNAAPTS) \cdot Py$

Compound (m.f.)	% Analysis, found (Calcd.) Ln	N	S	m.w. (Found (calcd.)	Λ_m (ohm^{-1} cm^2 mol^{-1})	μ_{eff} (BM)
$La(NO_3)_3 \cdot (HNAAPTS) \cdot Py$ ($C_{28}H_{27}N_{10}O_{10}SLa$)	16.54 (16.66)	16.58 (16.78)	3.79 (3.83)	830.0 (834.0)	2.1	Diamag.
$Pr(NO_3)_3 \cdot (HNAAPTS) \cdot Py$ ($C_{28}H_{27}N_{10}O_{10}SPr$)	16.74 (16.86)	16.55 (16.74)	3.77 (3.82)	832.0 (836.0)	1.9	03.59
$Nd(NO_3)_3 \cdot (HNAAPTS) \cdot Py$ ($C_{28}H_{27}N_{10}O_{10}SNd$)	17.04 (17.22)	16.49 (16.68)	3.76 (3.81)	833.0 (839.0)	1.8	03.57
$Sm(NO_3)_3 \cdot (HNAAPTS) \cdot Py$ ($C_{28}H_{27}N_{10}O_{10}SSm$)	17.60 (17.75)	16.38 (16.56)	3.73 (3.78)	841.0 (845.0)	2.0	01.60
$Gd(NO_3)_3 \cdot (HNAAPTS) \cdot Py$ ($C_{28}H_{27}N_{10}O_{10}SGd$)	18.30 (18.42)	16.24 (16.43)	3.70 (3.75)	847.0 (852.0)	1.9	07.82
$Tb(NO_3)_3 \cdot (HNAAPTS) \cdot Py$ ($C_{28}H_{27}N_{10}O_{10}STb$)	18.49 (18.61)	16.20 (16.39)	3.69 (3.74)	850.0 (854.0)	2.1	09.23
$Dy(NO_3)_3 \cdot (HNAAPTS) \cdot Py$ ($C_{28}H_{27}N_{10}O_{10}SDy$)	18.86 (18.95)	16.18 (16.32)	3.68 (3.73)	853.0 (857.5)	1.8	10.56
$Ho(NO_3)_3 \cdot (HNAAPTS) \cdot Py$ ($C_{28}H_{27}N_{10}O_{10}SHo$)	18.99 (19.18)	16.11 (16.27)	3.67 (3.72)	855.0 (560.0)	2.2	10.53

$Ln(NO_3)_3 \cdot (HNAAPTS) \cdot Py$ to that calculated is ~ 0.98, which shows that these complexes are monomeric in nature. In the case of $Ln(ClO_3)_3 \cdot 2(HNAAPTS) \cdot Py$, the ratio is found to be ~ 0.25. These data further support that four species are found in the perchlorate complexes.

The magnetic moment values of these complexes determined at room temperature (Tables I–IV) indicate that La(III) complexes are diamagnetic in nature, where Pr(III), Nd(III), Sm(III), Gd(III), Tb(III), Dy(III), and Ho(III) complexes are paramagnetic in nature. The values found are close to the theoretical values[8–10] and show little deviation from the Van Vleck values, indicating very little participation of the 4*f*-electrons in the bonding.

Infrared Spectra

The important infrared bands of free ligands (HNAAPTS and pyridine) and their lanthanides(III) are presented in Table V. The strong bands in the free ligand (HNAAPTS) observed at 3420 and 3310 cm^{-1} due to ν(NH) remained unaffected after complexation. The ligand bend at 1600 cm^{-1} (C=N of imine nitrogen) that shifted to lower wave numbers on complexation suggests involvement of an unsaturated nitrogen atom of two azomethine groups in bonding with the metal ion.[16] Other bands observed in the free ligand are at 1320, 1195 cm^{-1} due to $\nu(C{=}S) + \nu(C{=}N) + \nu(C{-}N)$, 1120, 1095 cm^{-1} due to $\delta(NCS)$ + CS bending, and 840, 820 cm^{-1} due to $\nu(C{=}S)$ stretching.[17] Coordination of sulfur with Ln^{3+} ion would result in displacement of electrons towards the latter, thus resulting in the weakening of (C=S) bond. Hence on complexation, (C=S) stretching vibrations should decrease and those of (C=N) should increase.[18] In the present complexes, the bands at 1320 and 1195 cm^{-1} increased by 50–60 cm^{-1}. Similarly, bending modes on (N—C—S) and (C=S) also increased, but to a lesser extent. On the other hand, on complexation the infrared bands at 840 and 820 cm^{-1} shifted to lower wave numbers

Table II Analytical, conductivity, molecular weight, and magnetic susceptibility of $LnCl_3 \cdot 2(HNAAPTS) \cdot Py$

	% Analysis, found (Calcd.)						
Compound (m.f.)	Ln	N	S	Cl	m.w. (Found (calcd.)	Λ_m (ohm^{-1} cm^2 mol^{-1})	μ_{eff} (BM)
$LaCl_3 \cdot 2(HNAAPTS) \cdot Py$ ($C_{51}H_{49}N_{13}O_2S_2Cl_3La$)	11.60 (11.73)	15.18 (15.36)	5.33 (5.40)	8.87 (8.99)	1179.0 (1184.5)	2.2	Diamag.
$PrCl_3 \cdot 2(HNAAPTS) \cdot Py$ ($C_{51}H_{49}N_{13}O_2S_2Cl_3Pr$)	11.63 (11.88)	15.16 (15.33)	5.34 (5.39)	8.85 (8.97)	1181.0 (1186.5)	2.4	3.42
$NdCl_3 \cdot 2(HNAAPTS) \cdot Py$ ($C_{51}H_{49}N_{13}O_2S_2Cl_3Nd$)	11.93 (12.10)	15.14 (15.30)	5.33 (5.38)	8.83 (8.95)	1183.0 (1189.5)	1.9	3.60
$SmCl_3 \cdot 2(HNAAPTS) \cdot Py$ ($C_{51}H_{49}N_{13}O_2S_2Cl_3Sm$)	12.38 (12.54)	15.08 (15.22)	5.30 (5.35)	8.80 (8.90)	1190.0 (1195.5)	2.5	1.61
$GdCl_3 \cdot 2(HNAAPTS) \cdot Py$ ($C_{51}H_{49}N_{13}O_2S_2Cl_3Gd$)	12.91 (13.05)	14.96 (15.13)	5.26 (5.32)	8.75 (8.85)	1196.0 (1202.5)	2.1	7.82
$TbCl_3 \cdot 2(HNAAPTS) \cdot Py$ ($C_{51}H_{49}N_{13}O_2S_2Cl_3Tb$)	13.03 (13.20)	14.95 (15.11)	5.27 (5.31)	8.76 (8.84)	1198.0 (1204.5)	2.3	9.49
$DyCl_3 \cdot 2(HNAAPTS) \cdot Py$ ($C_{51}H_{49}N_{13}O_2S_2Cl_3Dy$)	13.30 (13.44)	14.94 (15.05)	5.24 (5.29)	8.70 (8.81)	1203.0 (1208.0)	2.3	10.55
$HoCl_3 \cdot 2(HNAAPTS) \cdot Py$ ($C_{51}H_{49}N_{13}O_2S_2Cl_3Ho$)	13.44 (13.63)	14.90 (15.03)	5.23 (5.28)	8.69 (8.79)	1205.0 (1210.5)	1.8	10.51

Table III Analytical, conductivity, molecular weight, and magnetic susceptibility of Ln(NCS)$_3$·2(HNAAPTS)·Py

	% Analysis, found (Calcd.)						
Compound (m.f.)	Ln	N	S	NCS	m.w. (Found (calcd.)	Λ_m (ohm^{-1} cm^2 mol^{-1})	μ_{eff} (BM)
La(NCS)$_3$·2(HNAAPTS)·Py ($C_{54}H_{49}N_{16}O_2S_5La$)	10.93(11.10)	14.76(17.89)	12.53(12.77)	13.76(13.89)	1247.0(1252.0)	2.0	Diamag.
Pr(NCS)$_3$·2(HNAAPTS)·Py($C_{54}H_{49}N_{16}O_2S_5Pr$)	11.14(11.26)	17.63(17.86)	12.50(12.75)	13.75(13.87)	1249.0(1254.0)	2.1	3.40
Nd(NCS)$_3$·2(HNAAPTS)·Py ($C_{54}H_{49}N_{16}O_2S_5Nd$)	11.37(11.45)	17.62(17.82)	12.60(12.72)	13.69(13.84)	1252.0(1257.0)	1.9	3.59
Sm(NCS)$_3$·2(HNAAPTS)·Py ($C_{54}H_{49}N_{16}O_2S_5Sm$)	11.79(11.87)	17.55(17.73)	12.55(12.66)	13.64(13.77)	1257.0(1263.0)	2.1	1.63
Gd(NCS)$_3$·2(HNAAPTS)·Py ($C_{54}H_{49}N_{16}O_2S_5Gd$)	12.25(12.36)	17.45(17.63)	12.45(12.59)	13.58(13.70)	1265.0(1270.0)	2.2	7.92
Tb(NCS)$_3$·2(HNAAPTS)·Py ($C_{54}H_{49}N_{16}O_2S_5Tb$)	12.40(12.50)	17.44(17.61)	12.43(12.57)	13.53(13.67)	1266.0(1272.0)	2.3	9.29
Dy(NCS)$_3$·2(HNAAPTS)·Py ($C_{54}H_{49}N_{16}O_2S_5 \cdot Dy$)	12.63(12.74)	17.40(17.56)	12.42(12.54)	13.50(13.64)	1270.0(1275.5)	1.9	10.43
Ho(NCS)$_3$·2(HNAAPTS)·Py ($C_{54}H_{49}N_{16}O_2S_5Ho$)	12.79(12.91)	17.38(17.52)	12.38(12.51)	13.44(13.61)	1272.0(1278.0)	2.1	10.33

Table IV Analytical, conductivity, molecular weight, and magnetic susceptibility of $Ln(ClO_4)_3 \cdot 2(HNAAPTS) \cdot Py$

Compound (m.f.)	% Analysis, found (Calcd.)				m.w. (Found (calcd.)	Λ_m (ohm^{-1} cm^2 mol^{-1})	μ_{eff} (BM)
	Ln	N	S	ClO_4			
$La(ClO_4)_3 \cdot 2(HNAAPTS) \cdot Py$ ($C_{51}H_{49}N_{13}O_{14}S_2Cl_3La$)	9.90(10.09)	13.10(13.22)	4.59(4.65)	21.53(21.68)	345.0(1376.5)	74.9	Diamag.
$Pr(ClO_4)_3 \cdot 2(HNAAPTS) \cdot Py$ ($C_{51}H_{49}N_{13}O_{14}S_2Cl_3Pr$)	10.11(10.22)	13.08(13.20)	4.59(4.64)	21.52(21.65)	347.0(1378.5)	78.3	3.61
$Nd(ClO_4)_3 \cdot 2(HNAAPTS) \cdot Py$ ($C_{51}H_{49}N_{13}O_{14}S_2Cl_3Nd$)	10.32(10.42)	13.06(13.17)	4.58(4.63)	21.45(21.60)	348.0(1381.5)	77.8	3.57
$Sm(ClO_4)_3 \cdot 2(HNAAPTS) \cdot Py$ ($C_{51}H_{49}N_{13}O_{14}S_2Cl_3Sm$)	10.71(10.81)	12.98(13.11)	4.56(4.61)	21.38(21.51)	349.0(1387.5)	77.2	1.59
$Gd(ClO_4)_3 \cdot 2(HNAAPTS) \cdot Py$ ($C_{51}H_{49}N_{13}O_{14}S_2Cl_3Gd$)	11.16(11.25)	12.95(13.05)	4.53(4.59)	21.28(21.40)	350.0(1394.5)	79.1	7.85
$Tb(ClO_4)_3 \cdot 2(HNAAPTS) \cdot Py$ ($C_{51}H_{49}N_{13}O_{14}S_2Cl_3Tb$)	11.29(11.38)	12.90(13.03)	4.52(4.58)	21.28(21.37)	352.0(1396.5)	78.9	9.43
$Dy(ClO_4)_3 \cdot 2(HNAAPTS) \cdot Py$ ($C_{51}H_{49}N_{13}O_{14}S_2Cl_3Dy$)	11.50(11.60)	12.89(13.00)	4.52(4.57)	21.21(21.32)	353.0(1400.0)	77.8	10.62
$Ho(ClO_4)_3 \cdot 2(HNAAPTS) \cdot Py$ ($C_{51}H_{49}N_{13}O_{14}S_2Cl_3Ho$)	11.67(11.76)	12.88(12.97)	4.51(4.56)	21.16(21.28)	356.0(1402.5)	78.3	10.45

Table V Key infrared spectral bands (cm^{-1}) of mixed ligand complexes of lanthanides(III) with HNAAPTS and pyridine

Complex	ν(NH)	ν(C=N)	ν(C=S) + ν(C=N) + ν(C−N)	δ(NCS) + CS-bending	ν(N−N)	ν(C=S)	ν(C=C), ν(C=N) and ring vibrations	ν(Ln−N)/ ν(Ln−S)
HNAAPTS	3420s	1600vs	1320s	1120m	1060m	840s	—	—
	3310s		1195m	1095m		820s		
Pyridine	—	—	—	—	—	—	1597sh, 1583s	—
							1578s, 1483s	
							1439s	
LaCl$_3$·2(HNAAPTS)·Py	3420m	1575s	1365s	1170m	1070m	775s	1633s, 1610vs	430m
	3315m		1240m	1130m		755s	1510vs, 1465vs	320w
PrCl$_3$·2(HNAAPTS)·Py	3415m	1565s	1365s	1165m	1072m	770s	1630s, 1603vs	430m
	3312m		1248m	1125w		752s	1518vs, 1468vs	335w
NdCl$_3$·2(HNAAPTS)·Py	3422s	1570s	1362s	1172m	1068m	765s	1645s, 1605vs	422m
	3315s		1264m	1130m		750m	1490vs, 1480vs	325w
SmCl$_3$·2(HNAAPTS)·Py	3415m	1565s	1360s	1175m	1075m	770s	1635s, 1605vs	436m
	3317m		1230m	1130m		752m	1520vs, 1470vs	332w
GdCl$_3$·2(HNAAPTS)·Py	3420s	1568s	1370s	1165m	1065m	772m	1640s, 1610vs	422m
	3312m		1245s	1125w		755m	1500vs, 1482vs	322w
TbCl$_3$·2(HNAAPTS)·Py	3420m	1560s	1362s	1178m	1070m	772m	1642s, 1600vs	425m
	3310m		1240m	1132m		752m	1498vs, 1482vs	335w
DyCl$_3$·2(HNAAPTS)·Py	3416m	1562s	1365s	1170m	1068m	770s	1605sh, 1582s,	435m
	3312m		1240m	1132m		750s	1575s, 1470s	320w
HoCl$_3$·2(HNAAPTS)·Py	3420m	1650s	1360s	1172m	1072m	772s	1635s, 1612vs	442m
	3315m		1245m	1125m		700s	1520vs, 1470vs	330w
La(NO$_3$)$_3$·(HNAAPTS)·Py	3418m	1565s	1365s	1165m	1070m	770s	1645s, 1610vs	445m
	3305m		1240m	1125w		752s	1520vs, 1468vs	335w
Pr(NO$_3$)$_3$·(HNAAPTS)·Py	3415m	1560s	1360s	1170m	1060m	782m	1642s, 1608vs	437m
	3315m		1248m	1125m		755m	1523vs, 1470vs	332w
Nd(NO$_3$)$_3$·(HNAAPTS)·Py	3422m	1555s	1362s	1172m	1072m	772m	1645s, 1610vs	445m
	3310m		1232m	1130m		752m	1525vs, 1473vs	318w

(Continued on next page)

Table V Key infrared spectral bands (cm^{-1}) of mixed ligand complexes of lanthanides(III) with HNAAPTS and pyridine *(Continued)*

Complex	ν(NH)	ν(C=N)	ν(C=S) + ν(C=N) + ν(C−N)	δ(NCS) + CS-bending	ν(N−N)	ν(C=S)	ν(C=C), ν(C=N) and ring vibrations	ν(Ln−N)/ ν(Ln−S)
$Sm(NO_3)_3\cdot(HNAAPTS)\cdot Py$	3415m	1560s	1365s	1172m	1068m	765s	1635s, 1610vs	415w
	3312m		1240s	1125m		750m	1518vs, 1470vs	320w
$Gd(NO_3)_3\cdot(HNAAPTS)\cdot Py$	3423s	1562s	1362s	1168m	1070m	772m	1638s, 1612vs	440m
	3315s		1242m	1130w		755m	1520vs, 1472vs	330w
$Tb(NO_3)_3\cdot(HNAAPTS)\cdot Py$	3422s	1568s	1360s	1172m	1065m	765s	1645s, 1610vs	435m
	3315s		1248m	1132w		750m	1495vs, 1482vs	335w
$Dy(NO_3)_3\cdot(HNAAPTS)\cdot Py$	3422m	1565s	1362s	1178m	1072m	772s	1635s, 1612vs	440m
	3312m		1242s	1130m		755s	1500vs, 1480s	340w
$Ho(NO_3)_3\cdot(HNAAPTS)\cdot Py$	3415m	1568s	1370s	1172m	1065m	772m	1632s, 1605vs	435m
	3310m		1245m	1130m		752m	1505vs, 1482vs	335w
$La(NCS)_3\cdot 2(HNAAPTS)\cdot Py$	3418m	1570s	1362s	1165m	1070m	7565s	1642s, 1610vs	442m
	3310m		1240m	1125m		750m	1498vs, 1480s	325w
$Pr(NCS)_3\cdot 2(HNAAPTS)\cdot Py$	3415m	1565s	1365s	1172m	1068m	772m	1635s, 1608vs	435m
	3315m		1242m	1130m		752m	1518vs, 1470s	332w
$Nd(NCS)_3\cdot 2(HNAAPTS)\cdot Py$	3418m	1565s	1362m	1175m	1072m	770s	1600sh, 1585vs	440m
	3310m		1242m	1135m		752s	1578s, 1483s	340w
							1440s	
$Sm(NCS)_3\cdot 2(HNAAPTS)\cdot Py$	3415m	1560s	1370s	1172m	1070m	765s	1635s, 1612vs	430m
	3315m		1245m	1130m		750m	1515vs, 1465vs	335w
$Gd(NCS)_3\cdot 2(HNAAPTS)\cdot Py$	3410m	1562s	1365m	1170m	1065m	772m	1645s, 1605vs	435m
	3305m		1242m	1128m		752m	1518vs, 1468vs	320w
$Tb(NCS)_3\cdot 2(HNAAPTS)\cdot Py$	3420m	1568s	1360s	1172m	1068m	770m	1640s, 1605vs	425m
	3315m		1245m	1132m		752m	1522vs, 1472vs	315w

$Dy(NCS)_3 \cdot 2(HNAAPTS) \cdot Py$	3415m	1565s	1360m	1175m	1072m	782m	1642s, 1615vs	442m
	3312m		1240m	1130m		755m	1505vs, 1485vs	340w
$Ho(NCS)_3 \cdot 2(HNAAPTS) \cdot Py$	3416m	1575s	1362s	1165m	1075m	765m	1645s, 1608vs	435m
	3312m		1240m	1125w		752m	1492vs, 1478vs	335w
$La(ClO_4)_3 \cdot 2(HNAAPTS) \cdot Py$	3420m	1570s	1365s	1172m	1070m	772s	1640s, 1610vs	440m
	3310m		1245m	1128w		750m	1520vs, 1472vs	340w
$Pr(ClO_4)_3 \cdot 2(HNAAPTS) \cdot Py$	3422m	1572s	1370s	1168m	1072m	775m	1642s, 1602vs	445m
	3310m		1240m	1132w		755m	1498vs, 1482vs	342w
$Nd(ClO_4)_3 \cdot 2(HNAAPTS) \cdot Py$	3415m	1570s	1362m	1172m	1065m	765s	1635s, 1610vs	440m
	3310m		1245m	1130m		750m	1511vs, 1465w	340w
$Sm(ClO_4)_3 \cdot 2(HNAAPTS) \cdot Py$	3418m	1565s	1360s	1178m	1070m	772s	1632s, 1605vs	425w
	3310m		1230m	1132m		755m	1518vs, 1468vs	345w
$Gd(ClO_4)_3 \cdot 2(HNAAPTS) \cdot Py$	3415m	1575s	1362s	1165m	1072m	765s	1645s, 1608vs	430w
	3318m		1240m	1125m		752m	1492vs, 1480vs	340w
$Tb(ClO_4)_3 \cdot 2(HNAAPTS) \cdot Py$	3420m	1572s	1370s	1170m	1075m	772m	1635s, 1608vs	432w
	3312m		1245m	1128m		750m	1515vs, 1472vs	335w
$Dy(ClO_4)_3 \cdot 2(HNAAPTS) \cdot Py$	3418m	1562s	1365s	1175m	1072m	772s	1640s, 1615vs	435m
	3305m		1240m	1130m		755s	1522vs, 1472vs	325w
$Ho(ClO_4)_3 \cdot 2(HNAAPTS) \cdot Py$	3422m	1565s	1360s	1165m	1075m	765s	1645s, 16410vs	452m
	3315m		1248m	1125w		750m	1498vs, 1480vs	330w

with reduced intensity. All these peculiar changes on complexation confidently preclude any unambiguous ascertainment of metal-sulfur bonding. The possibility of thione-thiol tautomerism (H—N—C—S) (C—N—S—H) in HNAAPTS has been ruled out, for there were no bands around 2700–2500 cm^{-1}, which are characteristic of thiol groups displayed in the infrared absorption.[19] All the infrared spectral evidence suggested that the ligands, HNAAPTS acts as a neutral tridentate (N, N, S) in the lanthanide(III) complexes.

In the spectrum of pyridine, four strong absorptions occur in the range 1600–1400 cm^{-1} due to C=C, C=N stretching and ring vibrations.[20,21] Out of these, the absorptions associated with the cyclic ring are apparently unaffected on complexation, while those arising from the heterocyclic ring are shifted to higher frequencies due to tightening of the ring on coordination. This is suggestive of the view that the pyridine is bonded with the Ln^{3+} ion through the hetero-N atom.[22] In the far infrared region, the bands due to ν(Ln—N)/ν(Ln—S) are also observed.[9,10]

Anions

The infrared spectral data of nitrate absorptions in lanthanide(III) nitrate complexes are summarized in Table S1 (available online in the Supplemental Materials). The lanthanide(III) nitrate complexes show two a strong absorptions in the ~1525–1490 cm^{-1} and 1290–1280 cm^{-1} regions is attributed to ν_4 and ν_1 modes of vibration of the covalently bonded nitrate group, suggesting that the nitrate groups lie inside the coordination sphere.[23] Other absorptions associated with the covalent nitrate groups are also observed in the spectra of the complexes. If the (ν_4–ν_1) difference is taken as an approximate measure of the covalency of the nitrate groups, a value of ~200 cm^{-1} for the complexes studied suggest strong covalency for the metal nitrate bonding. According to Lever et al.,[24] bidentate coordination of nitrato groups involves a greater distortion from D_{3h} symmetry than unidentate coordination, therefore bidentate complexes should show a large separation of ($\nu_1+\nu_4$). Site symmetry lowering the coupling of the nitrato group via the metal ion to which they are coordinated to the occurrence of non-equivalent nitrato groups in the unit cells are some of the factors that may affect the occurrence of ($\nu_1+\nu_4$) combination bands. In the present studies, a separation of ~30–50 cm^{-1} in the combination bands in the 1800–1700 cm^{-1} region suggests the bidentate nitrate coordination. The bidentate character of the nitrato groups has been established by X-ray[25] and neutron diffraction studies.[26] Thus it is inferred that in the present studies the nitrate groups may be bidentate in nature. Complexes of the thiocyanate ion are known for most of the complexes formation of metal ions. According to the concepts of Pearson,[27] the N- end of this ion is a hard base, and the S- end a soft base. Consequently, N-bonding is expected with the hard (class-A) metal ions, while S-bonding should take place with those of soft category (class-B). The NCS$^-$ ion has been studied widely by infrared spectroscopy, which provides a means of establishing the bonding mode. Bailey et al.[28] suggested that the region near or above 2100 cm^{-1} is for S-bonding, below this value is for N-bonding. The CS stretching frequency (ν_2) was assigned in the following regions: 860–760 cm^{-1} for M—NCS and 720–690 cm^{-1} for M—SCN. The NCS frequency (ν_3) is also different for the two isomers: 490–450 cm^{-1} for the M—NCS and 440–400 cm^{-1} for M—SCN group. Bridging thiocyanate groups usually give higher CN stretching frequencies than terminal NCS groups. Table S2 (Supplemental Materials) shows the infrared absorption ν(C—N) (ν_1), ν(C—S) (ν_3), and δ(N—C—S) (ν_2). These frequencies are associated with the terminal N-bonded isothiocyanate ions.[29] In all the perchlorato complexes, only two strong ν_3 and ν_4 bands are observed in the 1090–1080 cm^{-1} and 625–620 cm^{-1}

regions, respectively (Table S3; Supplemental Materials), for the perchlorate ion, indicating that the tetrahedral symmetry has not been disturbed on complexation, and the perchlorate ions are not bonded to Ln^{3+} ion.[30,31] This conclusion is also supported by conductance and molecular weight data.

Electronic Spectra

Typical spectral data for the solutions of the present mixed ligand complexes of Ln^{3+} ion with HNAAPTS and pyridine are presented in Tables S4–S7 (Supplemental Materials), 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 regions appear due to transitions for the ground levels of $^3H_4$, $^4I_{9/2}$, $^6H_{5/2}$, $^5S_{7/2}$, and $_6H_{15/2}$ to the excited J-levels of the 4*f*-configuration, respectively. Some red shift or nephelauxetic effect is observed in the CH_3CN solutions of these complexes. This red shift is usually accepted as evidence of a higher degree of covalency than the presence of aquo compounds.[32] In all the complexes, marked enhancement in the intensity of the bands has been observed. This red shift of the hypersensitive bands has been utilized to calculate the nephelauxetic effect (β) in these chelates. From the β-values, the covalence factor ($b^{\frac{1}{2}}$), Sinha parameter ($\delta\%$), (metal–ligand covalency percentage), and the covalency angular overlap parameter (η) have been calculated. The positive values of (1-β) and $\delta\%$ in these compounds suggest that the bonding between the metal and the ligand is covalent compared to the bonding between the metal and an aquo ion. The values of parameter of bonding ($b^{\frac{1}{2}}$) and angular overlap parameter (η) were found to be positive, indicating covalent bonding.

$LnCl_3 \cdot 2(HNAAPTS) \cdot Py$ (Ln = La, Pr, Sm, or Dy). Thermoanalytical results of these compounds are presented in Table S8. The pyrolysis curves of these complexes indicate that in the 120–150°C temperature region, a loss of mass (6.76–6.92%) is due to complete evaporation of pyridine. There is no loss in mass up to 240°C, but in the 240–290°C temperature region, the loss of mass (42.63–43.40%) corresponds to loss of one molecule of HNAAPTS. A further loss of 78.26–79.86% in the temperature region shows the complete loss of HNAAPTS. The lanthanide oxide (La_2O_3, Pr_6O_{11}, Sm_2O_3, Dy_2O_3) was finally formed at ~ 820°C. Above this temperature, there is no measurable change in mass observed.[33]

$Ln(NO_3)_3 \cdot (HNAAPTS) \cdot Py$ (Ln = Pr, Sm, or Tb). Thermoanalytical results of these compounds are presented in Table S9 (Supplemental Materials). The pyrolysis curves of $Ln(NO_3)_3 \cdot (HNAAPTS) \cdot Py$ (Ln = Pr, Sm, or Tb) show that the compounds are anhydrous in nature. The thermal curves indicate that in the first stage, in the temperature region 120–155°C, there is a loss in mass (9.48–9.69%) due to loss of pyridine. In a second stage in the temperature region 240–360°C, the loss of (59.90–61.32%) is due to complete evaporation of HNAAPTS. Finally at ~ 825°C, the constant mass is close to that expected for lanthanide oxide (Pr_6O_{11}, Sm_2O_3, Tb_4O_7).[33]

$Ln(NCS)_3 \cdot 2(HNAAPTS) \cdot Py$ (Ln = Nd, Dy, or Ho). The analysis of pyrolysis data on these complexes are tabulated in Table S10 (Supplemental Materials). The thermograms of these complexes indicate virtually no change in mass up to 120°C. In the temperature zone of 120–145°C, a loss of 6.40–6.52% is observed due to complete loss of pyridine. In the 230–285°C temperature range, the loss in mass (40.28–41.22%) is due to removal of one molecule of HNAAPTS. A further loss in mass (74.84–76.10%) in the

310–340°C temperature region is due to complete evaporation of HNAAPTS. The residues obtained after heating up to $\sim$ 825°C to constant mass are close to those expected for the lanthanide oxides (Nd_2O_3, Dy_2O_3 or Ho_2O_3).[33]

Stereochemistry

[Ln(HNAAPTS)(NO_3)$_3$·Py] (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho). The conductance measurement of these compounds in nitrobenzene indicates the non-ionic nature of these species. Hence all three nitrate groups are present inside the coordination sphere. Infrared data reveals the bidentate nature of NO^{3}_{-}. HNAAPTS is a neutral tridentate (N, N, S) ligand, and pyridine is coordinated to the N-atom. Thus lanthanide ions are surrounded by six oxygen atoms, three nitrogen atoms, and 1 sulfur atom, thus producing a coordination number of 10 for the lanthanide ion[34] (Figure 2a).

[Ln(HNAAPTS)$_2$$Cl_3$·Py] (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho). The non-electrolytic behavior of the chloro complexes suggest that all the chloro ions are present in coordination sphere. HNAAPTS is a neutral tridentate ligand (N, N, S) and pyridine is coordinated to the central metal ion through heterocyclic-N atom. Thus lanthanide ions are surrounded by three chloro, five nitrogen, and two sulfur atoms, thus producing a coordination number 10 for the lanthanide ion[34] (Figure 2b).

[Ln(HNAAPTS)$_2$(NCS)$_3$·Py] (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho). The non-electrolytic behavior and infrared studies of these chelates suggests that all the NCS ions are coordinated to the Ln^{3+} ion via the N-atom. HNAAPTS is a neutral tridentate ligand (N, N, S-donor), and pyridine is a neutral N-donor ligand, thus a coordination number 10 for the lanthanide ion has been suggested in all these compounds[34] (Figure 2c).

[Ln(HNAAPTS)$_2$Py](ClO_4)$_3$ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho). The molar conductance of these compounds in nitrobenzene indicates that they behave as 1:3 electrolyses. Hence none of the 3-ClO^{4}_{-} is bonded to the central Ln^{3+} ion, and they are present outside the coordination sphere. Infrared spectra and thermal studies further indicate the absence of either aquo ligand or ethanol and, hence, a coordination number of 7 has been assigned in these compounds[34] (Figure 2d).

EXPERIMENTAL

The lanthanide chloride nitrate and oxides were obtained from Rare Earth Products Ltd. (India) and were used without further purification. The lanthanide perchlorates were prepared by heating the corresponding oxides with perchloric acid and evaporating off the excess acid. The lanthanide isothiocyanates were prepared by adding a warm ethanolic solution of KCNS. The precipitate of KNO_3 rapidly coagulated. The volume of the solution was reduced on a water bath, cooled, and filtered, and the filtrate was used for complexation. The ligand HNAAPTS was synthesized from 4-aminoantipyrine by the method reported in the literature.[11] The secondary ligand pyridine was obtained from Aldrich Chemical and used as received.

Synthesis of the Complexes

All the complexes were prepared in non-aqueous media and isolated as solids by different methods described below:

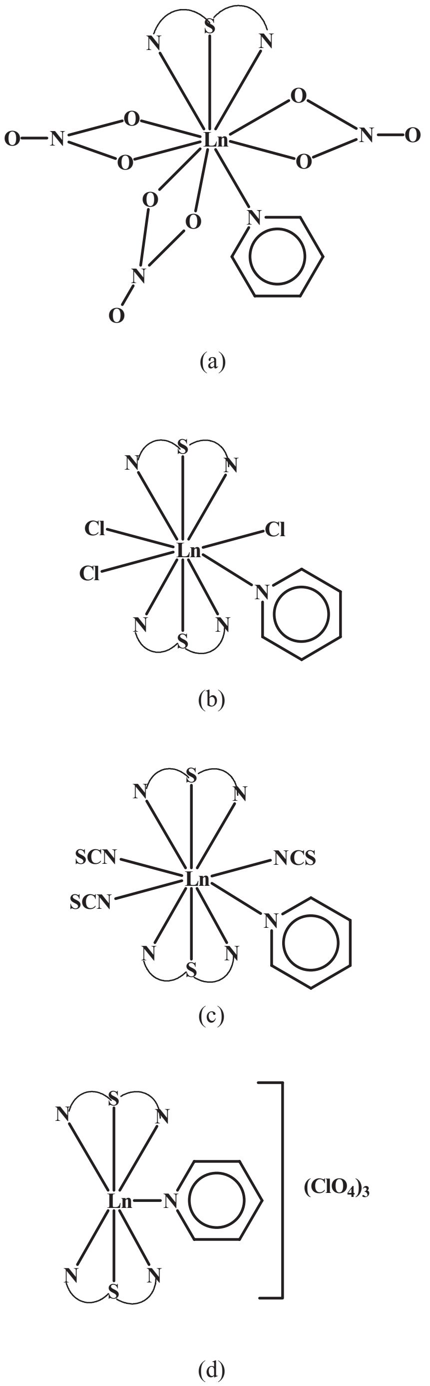

Figure 2 Proposed structure of lanthanide(III) complexes of HNAAPTS and pyridine. (a) [Ln (HNAAPTS)(NO_3)$_3$·Py], (b) [Ln(HNAAPTS)$_2$$Cl_3$·Py], (c) [Ln(HNAAPTS)$_2(NCS)_3$·Py], (d) [Ln(HNAAPTS)$_2$·Py]($ClO_4$)$_3$.

(i). $Ln(NO_3)_3 \cdot (HNAAPTS) \cdot Py$ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho). All these nitrato complexes were prepared by mixing the methanolic solutions of the respective lanthanide(III) nitrate (1 mmol, 0.325–0.351g in methanol, 10 mL), HNAAPTS (1 mmol, 0.407 g in methanol, 10 mL), and pyridine (1 mmol, 0.079 g in methanol, 10 mL) in the molar ratio 1:1:1 and refluxing the resulting mixture for ca. 3 h. The resulting solution was concentrated by evaporation on a water bath the left overnight. The yellow product was separated by filtration, washed with hot methanol, and dried in vacuo over P_4O_{10}.

(ii). $LnCl_3 \cdot 2(HNAAPTS) \cdot Py/Ln(NCS)_3 \cdot 2(HNAAPTS) \cdot Py$ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho). The corresponding lanthanide(III) chloride (1 mmol, 0.245–0.271 g in methanol, 10 mL)/lanthanide(III) thiocyanate (1 mmol, 0.313–0.339 g in methanol, 10 mL) and ligands [HNAAPTS (2 mmol, 0.814 g in 20 mL of methanol) and pyridine (1mmol, 0.079 g in methanol, 10 mL)] were taken in 1:2:1 molar ratio (all in hot methanol), and the reduction mixture was refluxed for ~ 2–3 h on a water bath. The reaction mixture was then concentrated on a water bath until a precipitate was obtained (digested for ~ 0.5 h), then it was filtered, washed thoroughly with methanol and finally with anhydrous diethyl ether, and dried over P_4O_{10} in a vacuum desiccator.

(iii). $Ln(ClO_4)_3 \cdot 2(HNAAPTS) \cdot Py$ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, or Ho). Lanthanide(III) perchlorate (1 mmol, 0.438–0.464 g in methanol, 10 mL), HNAAPTS (2mmol, 0.814 g in methanol, 20 mL), and pyridine (1mmol, 0.079 g in methanol, 10 mL) were placed in a 100 mL capacity round bottom flask. The reaction mixture was refluxed for ~ 3 h, and the resulting solution was concentrated to a viscous mass. It was washed several times with small portions of hot benzene, and finally the solid mass was washed with anhydrous diethyl ether, collected, and dried over P_4O_{10}.

Physical Measurements and Analytical Estimations

The metal content was estimated as its oxide by direct combustion in a platinum crucible. The estimation was further confirmed by dissolving the product of direct combustion in dil. HCl. The acid extract was transferred into a flask, and the pH was adjusted to 5.8–6.4 by the addition of an acetic acid–sodium acetate buffer and was then titrated against 0.1 M–EDTA using xylenol-orange as an indicator. The results from both the methods were compared and found to be within the experimental errors. The nitrogen contents of the compounds were estimated by the Kjeldahl method in the laboratory. The percentage of sulfur was estimated in the laboratory by standard method. The perchlorate was estimated by the method as suggested by Kurz et al.,[12] and the chloro and thiocyanato were determined by Volhard's method. The molecular weight of the complexes was determined cryoscopically in freezing nitrobenzene using a Beckmann thermometer of accuracy ± 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 nitrobenzene. The magnetic measurements were carried out at room temperature with a Gouy's balance and $[HgCo(SCN)_4]$ was used as a calibrant. The infrared spectra of the complexes were recorded on a Perkin-Elmer infrared spectrophotometer model in KBr in the range of 4000–200 cm^{-1}. A higher Uvispeck spectrophotometer with 1 cm quartz cell was employed for recording the visible spectra of the complexes. The red shift of the hypersensitive bands has been utilized to calculate the nephelauxetic effect (β) in these chelate compounds. From the β-values, the covalence factors ($b^{\frac{1}{2}}$), Sinha parameters ($\delta\%$) (metal–ligand covalency percentage) and the covalency angular overlap parameter (η) have been calculated by the following equations:[13,14]

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

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

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

Thermogravimetric analysis of lanthanide(III) chelate compounds was carried out in static air with open sample holder and a small platinum boat, and the heating rate was 6°/min.

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