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SHORT COMMUNICATION

SYNTHESIS AND PRELIMINARY STRUCTURAL CHARACTERIZATION OF SOME LANTHANIDE(III) SEMICARBAZONE COMPLEXES

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ABSTRACT. Some six and nine coordinated complexes of trivalent lanthanide metal ions with 4[N-(2'-hydroxy-1'-naphthalidene)amino]antipyrinesemicarbazone (HNAAPS) with the general composition $LnX_3.n$(HNAAPS) [X = NO_3, n = 1; X = NCS or ClO_4, n = 2; Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho] have been isolated. All the complexes have been characterized on the basis of analytical data, molar conductance, magnetic susceptibility, electronic and infrared spectral measurements. The ligand HNAAPS behaves as neutral tridentate (N, N, O) ligand. The coordination number of the central metal ion is either six or nine in these complexes. Thermal properties of these complexes were also investigated.

KEY WORDS: Lanthanide(III) complexes, 4[N-(2'-hydroxy-1'-naphthalidene)amino]antipyrine semicarbazone

INTRODUCTION

Thiosemicarbazones and their metal complexes have been the subject of extensive investigations because of their potential pharmacological properties and a wide variation in their modes of bonding and stereochemistry [1-3], whereas their semicarbazones analogs received much less attention [4-8]. However, semicarbazones are reported to possess versatile structural features [9] and very good antifungal and antibacterial properties [10, 11]. In view of this, we describes herein the synthesis and magneto-spectral properties of some six and nine coordinated complexes of lanthanides(III) derived from 4[N-(2'-hydroxy-1'-naphthalidene)amino]antipyrine semicarbazone (HNAAPS) (Figure 1). All the complexes were characterized by molar conductivity, molar mass, magnetic susceptibility, infrared and electronic spectra.

EXPERIMENTAL

The lanthanide nitrates 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 (A.R.) and evaporating the excess acid [12]. The lanthanide thiocyanates were prepared by adding a warm ethanolic solution of lanthanide nitrates to warm ethanolic solutions 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 [13]. The ligand HNAAPS was synthesized by the reported method [7, 8]. The chemical analyses and physico-chemical measurements were performed as reported earlier [14, 15].

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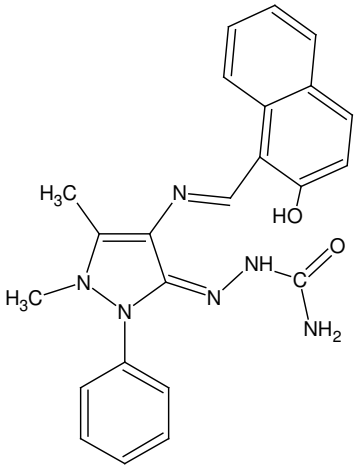

Figure 1. Structure of 4[N-(2′-hydroxy-1'-naphthalidene)amino]antipyrinesemicarbazones (HNAAPS).

Synthesis of the complexes

$Ln(NO_3)_3$.(HNAAPS) (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho). A solution containing lanthanide(III) nitrate and HNAAPS in 1:1 molar ratio in hot methanol stirred on a hot plate for ~ 2 h. On cooling the precipitate was obtained, which was separated by centrifugation. The precipitate was washed several times with methanol to remove any unreacted ligand and the metal salt and dried in vacuo over P_4O_{10}.

$Ln(NCS)_3$.2(HNAAPS) (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho). The isothiocyanate complexes were prepared by adding 40 mL of hot methanol solution of HNAAPS (2 mmol) to the ethanolic solution of lanthanide(III) isothiocyanate (1 mmol) and the reaction mixture was refluxed for 1 h on a water bath. The reaction mixture was then concentrated, until a precipitate was obtained. It was digested for about 10 min and filtered. The precipitate was washed thoroughly with methanol and diethyl ether and finally dried over P_4O_{10} in a vacuum desiccator.

[$Ln(ClO_4)_3$.2(HNAAPS)] (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho). The solutions of lanthanide(III) perchlorate (1 mmol) and HNAAPS (2 mmol) in hot methanol were mixed and refluxed on a water bath for ~ 2 h. It was then concentrated to about half of the original solution. About 20 mL of diethyl ether was added in cold concentrated solution with constant stirring to separate the desired complex. It was collected and washed with diethyl ether and finally dried under vacuum over P_4O_{10}.

RESULTS AND DISCUSSION

The reaction of non-aqueous solutions of lanthanide(III) salts with 4[N-(2'-hydroxy-1'-naphthalidene)amino]antipyrinesemicarbazone (HNAAPS) produced complexes with the general composition $LnX_3.n$(HNAAPS) [X = NO_3, n =1; X = NCS or ClO_4, n = 2; Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho]. The complexes are quite stable and are generally soluble in

common organic solvents, but insoluble in diethyl ether. Thermogravimetric studies confirm the absence of either coordinated or uncoordinated water molecule in these complexes. The molar conductance of nitrato and isothiocyanato complexes in nitrobenzene revealed the complexes to be non-electrolytes. In contrast the perchlorato complexes behave as 1:3 electrolytes in nitrobenzene. From elemental analysis studies the ratio of observed over calculated molecular weights for $[Ln(NO_3)_3(HNAAPS)]$ or $[Ln(NCS)_3.2(HNAAPS)]$ gave a value of ~ 0.98, which shows that the complexes are monomeric in solution. In the case of $Ln(ClO_4)_3.2(HNAAPS)$, the ratio is found to be ~ 0.25, which led us to propose the formation of four species in the perchlorato complexes.

Magnetic studies. The magnetic moment studies confirm that lanthanum complexes are diamagnetic in nature, as expected from its closed shell electronic configuration and absence of unpaired electrons. All other tripositive lanthanide complexes are paramagnetic due to the presence of $4f$ electrons, which are effectively shielded by $5s^2$ and $5p^6$ electrons. Similar observation has been reported previously [14, 15].

Infrared spectra. Vibrational studies conducted on the complexes show the absence of $\nu(NH_2)$ of the hydrazinic nitrogen of semicarbazide (~ 1622 cm^{-1}) in the infrared spectra of the HNAAPS [7, 8]. The characteristic absorption of the carbonyl group in HNAAPS is observed [7, 8] at 1700 cm^{-1}. In all the complexes, this band is shifted toward lower energy region of 1652-1640 cm^{-1}. The amide-II band in free HNAAPS has been observed at 1560 cm^{-1}. In all the present complexes of HNAAPS, 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 1605 cm^{-1} in HNAAPS apparently has a large contribution from the ν(C=N) band in all the complexes as compared to the free ligand. Another strong band was observed at 1620 cm^{-1} due to azomethine (C=N) absorption. On complexation this band is shifted towards the low frequency region, clearly indicating the coordination through the azomethine N-atom [7, 8]. In far infrared region the bands due to ν(Ln-N)/ν(Ln-O) are also observed [14-17]. In free ligand, the stretching frequency in 3400-3300 cm^{-1} region is attributed to ν(OH). In all the complexes of HNAAPS, the –OH absorption bands appeared in the same region as in free HNAAPS clearly indicating that the –OH group is not taking part in the coordination. The above discussion clearly indicates that HNAAPS serves as tridentate ligand coordinating through the carbonyl-O, hydrazinic-N and azomethinic-N atoms.

The nitrato complexes exhibited the occurrence of two strong absorptions at 1525-1515 cm^{-1} and 1310-1290 cm^{-1} region attributed to ν_4 and ν_1 modes of vibration of covalently bonded nitrate group, respectively, suggesting that the nitrate groups lie inside the coordination sphere [17]. Other absorptions associated with the covalent nitrate groups are also observed in the spectra of the metal complexes. If the (ν_4 - ν_1) difference is taken as an approximate measure of the covalency of the nitrate groups [17], a value of ~ 200 cm^{-1} for the complexes studied herein suggest strong covalency for the metal-nitrate bonding. To identify the monodentate or bidentate nature of NO_3^- group, we applied Lever separation method [18]. In present complexes, the separation of ~ 30-40 cm^{-1} in the combination bands (ν_4 + ν_1) in the 1800-1700 cm^{-1} region conclude the bidentate nitrate coordination. In all the thiocyanate complexes, all the three fundamental absorptions ν(CN) (ν_1), ν(CS) (ν_2) and δ(NCS) (ν_3) are identified in 2065 – 2045, 830-760, and 480-475 cm^{-1}, respectively, which are associated with the terminal N-bonded isothiocyanate ion [19, 20]. The occurrence of two strong bands in 1090-1080 cm^{-1} and 625-620 cm^{-1} region in the spectra of $Ln(ClO_4)_3.2(HNAAPS)$ attributed to ν_3 and ν_4 vibrations of the ionic perchlorate suggest that all the perchlorato groups are present outside the coordination sphere [19].

Electronic spectra. Electronic spectral data of the solutions of the trivalent lanthanide complexes in CH_3CN were compared with those of the aquo salt solution. Lanthanum(III) has no significant absorption in the visible region. The absorption bands of praseodymium(III), neodymium(III) and samarium(III) in the visible and infrared region appear due to transitions from the ground levels $^3H_4$, $^4I_{9/2}$, $^6H_{5/2}$ to the excited J-levels of 4*f* configuration, respectively. Some red shifts or nephelauxetic effect is observed in CH_3CN solution of these complex compounds. This red shift is usually accepted as evidence of a higher degree of covalency than existing in the aquo compounds [21]. In all the complexes 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 (δ %), *i.e.* metal-ligand covalency percent and the covalency angular overlap parameter (η) have been calculated [21, 22].

The positive values for (1-β) and δ % in these coordination compounds (Tables 1-3) suggest that the bonding between the metal and the ligand is covalent as compared with the bonding between the metal and an aquo ion. The values of parameter of bonding ($b^{1/2}$) and angular overlap parameter (η) were found to be positive indicating covalent bonding.

Table 1. Eelectronic spectral data (cm^{-1}) and related bonding parameters of lanthanide(III) nitrate complexes of HNAAPS.

Ln^{3+}	$Ln(NO_3)_3$ electronic spectral band	[Ln(HNAAPS) $(NO_3)_3$] electronic spectral bands	*J*-Levels	(1-β)	β	$b^{1/2}$	δ%	η
Pr^{3+}	22,470	22,320	$^3H_4 \rightarrow {}^3P_2$	0.00667	0.99332	0.04083	0.67148	0.00335
	21,280	21,200	$\rightarrow {}^3P_1$	0.00845	0.99154	0.04596	0.86128	0.00425
	20,830	20,650	$\rightarrow {}^3P_0$	0.00864	0.99135	0.04647	0.87153	0.00435
	16,950	16,750	$\rightarrow {}^1D_2$	0.01179	0.98820	0.05429	1.19307	0.00591
Nd^{3+}	19,420	19,250	$^4I_{9/4} \rightarrow {}^2G_{9/2}$	0.00875	0.99124	0.04677	0.88273	0.00440
	17,390	17,200	$\rightarrow {}^4G_{5/2}, {}^2G_{7/2}$	0.01092	0.08007	0.05224	1.10406	0.00551
	13,420	13,200	$\rightarrow {}^2S_{3/2}, {}^4F_{7/2}$	0.01639	0.98360	0.06401	1.66632	0.00823
	12,500	12,350	$\rightarrow {}^4F_{5/2}, {}^4H_{9/2}$	0.01200	0.98800	0.05477	1.21457	0.00601
Sm^{3+}	24,850	24,700	$^4H_{5/2} \rightarrow {}^4P_{9/2}$	0.00603	0.99396	0.03882	0.60666	0.00303
	24,100	23,800	$\rightarrow {}^6P_{5/2}$	0.01244	0.98755	0.05576	1.25968	0.00628
	21,600	21,440	$\rightarrow {}^4P_{13/2}$	0.00740	0.99259	0.04301	0.74552	0.00372

Table 2. Electronic spectral data (cm^{-1}) and related bonding parameters of lanthanide(III) isothiocyanate complexes of HNAAPS.

Ln^{3+}	$Ln(NCS)_3$ electronic spectral bands	[Ln(HNAAPS) $(NCS)_3$] electronic spectral bands	*J*-Levels	(1-β)	β	$b^{1/2}$	δ%	η
Pr^{3+}	22,400	22,520	$^3H_4 \rightarrow {}^3P_2$	0.00669	0.99330	0.04089	0.67351	0.00710
	21,230	21,050	$\rightarrow {}^3P_1$	0.00847	0.99152	0.04601	0.85424	0.00426
	20,800	20,620	$\rightarrow {}^3P_0$	0.00865	0.99134	0.04650	0.87255	0.00435
	16,900	16,720	$\rightarrow {}^1D_2$	0.01065	0.98934	0.05159	1.07647	0.00534
Nd^{3+}	19,400	19,210	$^4I_{9/4} \rightarrow {}^2G_{9/2}$	0.00979	0.99020	0.04947	0.98868	0.00493
	17,400	17,200	$\rightarrow {}^4G_{5/2}, {}^2G_{7/2}$	0.01149	0.98850	0.05359	1.16236	0.00580
	13,400	13,250	$\rightarrow {}^2S_{3/2}, {}^4F_{7/2}$	0.01119	0.98881	0.05289	1.13167	0.00564
	12,500	12,220	$\rightarrow {}^4F_{5/2}, {}^4H_{9/2}$	0.02240	0.97760	0.07483	2.29132	0.01127
Sm^{3+}	24,900	24,700	$^4H_{5/2} \rightarrow {}^4P_{9/2}$	0.00803	0.99196	0.04480	0.80950	0.00404
	24,000	23,820	$\rightarrow {}^6P_{5/2}$	0.00750	0.99250	0.04330	0.75566	0.00377
	21,600	21,440	$\rightarrow {}^4P_{13/2}$	0.00740	0.99260	0.04301	0.74552	0.00372

Table 3. Electronic spectral data (cm^{-1}) and related bonding parameters of lanthanide(III) perchlorato complexes of HNAAPS.

Ln^{3+}	$Ln(ClO_4)_3$ electronic spectral bands	[Ln(HNAAPS)$(ClO_4)_3$] electronic spectral bands	*J*-Levels	(1-β)	β	$b^{1/2}$	δ%	η
Pr^{3+}	22,470	22,340	$^3H_4 \rightarrow {}^3P_2$	0.00578	0.99421	0.03801	0.58136	0.00290
	21,325	21,200	$\rightarrow {}^3P_1$	0.00586	0.99413	0.03827	0.58946	0.00294
	20,750	20,620	$\rightarrow {}^3P_0$	0.00625	0.99373	0.03956	0.62994	0.00315
	17,000	16,850	$\rightarrow {}^1D_2$	0.00882	0.99117	0.04695	8.8985	0.00444
Nd^{3+}	19,600	19,450	$^4I_{9/4} \rightarrow {}^2G_{9/2}$	0.00765	0.99234	0.04373	0.77090	0.00385
	17,380	17,250	$\rightarrow {}^4G_{5/2}, {}^2G_{7/2}$	0.00747	0.99252	0.04321	0.75262	0.00376
	13,680	13,580	$\rightarrow {}^2S_{3/2}, {}^4F_{7/2}$	0.00730	0.99270	0.04272	0.73536	0.00367
	12,470	12,380	$\rightarrow {}^4F_{5/2}, {}^4H_{9/2}$	0.00721	0.99278	0.04245	0.72624	0.00362
Sm^{3+}	24,870	24,740	$^4H_{5/2} \rightarrow {}^4P_{9/2}$	0.00522	0.99477	0.03612	0.52474	0.00261
	24,000	23,800	$\rightarrow {}^6P_{5/2}$	0.00833	0.99166	0.04563	0.84000	0.00419
	21,550	21,450	$\rightarrow {}^4P_{13/2}$	0.00464	0.99535	0.03405	0.46616	0.00233

Thermogravimetric studies

[Ln(NO$_3$)$_3$.(HNAAPS)] (Ln = La, Pr or Gd). The pyrolysis curves of [Ln(NO$_3$)$_3$.(HNAAPS)] (Ln = La, Pr or Gd) show that the complexes are anhydrous in nature. The thermal curves indicate that at ~ 245 ^oC, the compounds start to loose mass with a partial evaporation of organic ligand up to temperature of 360 ^oC. The residues obtained after heating at ~ 840 ^oC to the constant weight is very close to that of expected for lanthanide oxides (La_2O_3, Pr_6O_{11} and Gd_2O_3) [14, 15, 23].

[Ln(NCS)$_3$.2(HNAAPS)] (Ln = La, Pr,Gd or Tb). The pyrolysis curves of these complexes indicate that at ~ 200 ^oC, the complexes start to loose mass with partial evaporation of the organic ligand up to a temperature of 310 ^oC. The loss of mass (34.42-36.19 %) corresponds to one mole of HNAAPS. At 410 ^oC, the remaining HNAAPS is also lost. The residue obtained after heating at ~ 830 ^oC to constant weight is very close to that of expected for lanthanide oxides [14, 15, 23].

[Ln(ClO$_4$)$_3$.2(HNAAPS)] (Ln = La, Gd or Dy). The thermograms of these complexes indicate that there is no virtually change in weight up to 190 ^oC. At the temperature region of 190 - 225 ^oC, a loss of 31.86 - 32.26 % is observed which corresponds to one mole of the organic ligand followed by a further loss of 64.08 - 64.89 % in 250 - 300 ^oC temperature region showing the complete loss of HNAAPS. The lanthanide oxide (Nd_2O_3, Gd_2O_3 or Dy_2O_3) was finally formed at ~ 835 ^oC. Above this temperature, there is no measurable change in the weight [14, 15, 23].

CONCLUSION

The conductance measurements of [LnNO$_3$)$_3$.(HNAAPS)] (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho) in nitrobenzene indicate the non-ionic nature of these species. Hence all the three nitrate groups are presumed to be present inside the coordination sphere. Infrared studies reveal the bidentate nature of NO_3^- and the presumed coordination of HNAAPS to the central metal ion in tridentate (N,N,O) modes. Thus lanthanide ions are expected to be surrounded by seven-oxygen and two-nitrogen atoms. Hence a coordination number of nine is assigned for the lanthanide atom in these coordination complexes [24]. For [Ln(NCS)$_3$.2(HNAAPS)] (Ln = La, Pr, Nd, Sm,

Gd, Tb, Dy or Ho), the non-electrolytic behavior of these complexes suggests that all the NCS^- ions are coordinated to the central metal ion [25]. The infrared spectral data indicate that the lanthanide ions are surrounded by seven nitrogen atoms (three N- of isothiocyanate ions and four N- of the HNAAPS) and two oxygen atoms of the amide group of HNAAPS. Hence a coordination number of nine for La, Pr, Nd, Sm, Gd, Tb, Dy or Ho has been suggested in these complexes. In case of $[Ln(HNAAPS)_2](ClO_4)_3$ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho) complexes the molar conductance values in nitrobenzene indicate that the complexes behave as 1:3 electrolytes. Hence all the three perchlorato ions are not bonded to the lanthanides and present outside the coordination sphere. It is further confirmed by infrared studies. Infrared spectra further indicate the absence of water/solvent in present perchlorato complexes. Hence a coordination number six to the lanthanide ion has been assigned in all these complexes [25].

REFERENCES

1. Agarwal, R.K.; Prasad, S.; Gahlot, N. *Turk. J. Chem.* **2004**, 28, 691.
2. Agarwal, R.K.; Prasad, S. *Turk. J. Chem.* **2005**, 29, 289
3. Agarwal, R.K.; Garg, R.K.; Sindhu, S.K. *Bull. Chem. Soc. Ethiop.* **2005**, 19, 185.
4. Agarwal, R.K. *Chimica Acta Turcica* **2004**, 32, 19.
5. Agarwal, R.K.; Prakash, B. *Chimica Acta Turcica* **2004**, 32, 25.
6. Agarwal, R.K.; Prasad, S. *J. Iranian Chem. Soc.* **2005**, 2, 168
7. Agarwal, R.K.; Chakraborti, I.; Agarwal, H. *Synth. React. Org. Met.-Inorg. Chem.* **2004**, 34, 1431.
8. Agarwal, R.K.; Chakraborti, I.; Agarwal, H. *Synth. React. Org. Met.-Inorg. Chem.* **2004**, 34, 1453.
9. Akkurt, M.; Ozfuric, S.; Ide, S. *Anal. Sci.* **2000**, 16, 667.
10. Dimmock, J.R.; Puthucode, R.N.; Smith, J.M.; Hetherington, M.; Quail, J.W.; Pugazhenthi, U. *J. Med. Chem.* **1996**, 39, 3984 .
11. Dimmock, J.R.; Sidhu, K.K.; Tumber, S.D.; Basran, S.K.; Chen, M.; Quail, J.W. *J. Med. Chem.* **1995**, 30, 287.
12. Sandhu, S.S.; Aulakh, G.S. *Indian J. Chem.* **1974**, 12**,** 1102.
13. Cousin, D.R.; Hart, F.A. *J. Inorg. Nucl. Chem.* **1968**, 30, 3009.
14. Agarwal, R.K.; Sarin, R.K. *Synth. React. Inorg. Met.-Org. Chem.* **1994**, 24**,** 185, 499.
15. Agarwal, R.K.; Agarwal, H. *Synth. React. Inorg. Met.-Org. Chem.* **2001**, 31, 263.
16. Radhakrishna, P.S.; Indrasenan, P.; Nair, C.G.R. *Polyhedron* **1984**, 3**,** 67.
17. Agarwal, R.K.; Agarwal, H.; Manglik, A.K. *Synth. React. Inorg. Met.-Org. Chem.* **1996**, 26**,** 1163 .
18. Lever, A.B.P.; Mantiovani, E.; Ramaswamy, B.S. *Canad. J. Chem*. **1977**, 49, 1957.
19. Nakamoto, K. *Infrared spectra of inorganic and coordination compounds*, Wiley: New York; **1970**.
20. Burmeister, J.L. *Coord. Chem. Rev.* **1966**, 1**,** 205; **1968**, 3, 225; **1990**, 105, 77.
21. Sinha, S.P. *Spectrochim. Acta* **1966**, 22, 57.
22. Tandon, S.P.; Mehta P.C. *J. Chem. Phys.* **1970**, 52, 4313.
23. Agarwal, R.K.; Gupta, S.K. *Thermochim. Acta* **1985**, 95**,** 99.
24. Koppikar, D.K.; Sivapulliah P.V.; Ramakrishna L.; Soundararajan S. *Struct. Bond.* **1978,** 34, 135.
25. Singh, L.; Sharma, A.K.; Sindhu, S.K. *Asian J. Chem.* **1999**, 11, 1445.