

## SHORT COMMUNICATION

### SYNTHESIS AND SPECTRAL STUDIES OF SOME LANTHANIDE(III) COMPLEXES WITH 4-[N-(*p*-DIMETHYLAMINO BENZALIDENE)AMINO] ANTIPYRINE SEMICARBAZONE

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(Received January 15, 2001; revised May 10, 2001)

**ABSTRACT.** In the present work, we describe the isolation of some lanthanide(III) complexes of 4-[N-(*p*-dimethylaminobenzalidene)amino]antipyrine semicarbazone (DABAAPS) with general composition  $[Ln(DABAAPS)_2X_3]$  (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho and X = Cl<sup>-</sup> and NCS<sup>-</sup>). All the isolated compounds were characterized through various physico-chemical studies. The coordinating ligand DABAAPS behave as tridentate N,N,O-donors. The central metal ion displays the coordination number nine in these complexes. Thermal stabilities of these complexes were also studied through thermogravimetric analysis.

**KEY WORDS:** Lanthanide(III) complexes, 4-[N-(*p*-Dimethylaminobenzalidene)amino]antipyrine semicarbazone, Tridentate N,N,O-donors

## INTRODUCTION

The coordination number exhibited by the lanthanide ions generally varies from six to ten; bidentate ligands with a smaller bite often yield complexes with higher coordination numbers [1]. Some years ago, the crystal structure of hexakis(1,8-naphthyridine)praseodymium perchlorate was reported and shown to involve a twelve coordinated praseodymium molecule [2]. As the 4f-orbitals are sufficiently shielded by external "shells" as to be largely unavailable for bonding with the ligand orbitals, they do not have any bond orienting character. As a result, the structure of a lanthanide complex is dictated by the following consideration [1]: (a) preserving a spherical symmetry for the central metal ion, (b) minimizing ligand-ligand and metal-metal repulsion, and (c) steric requirements of the ligands.

Recently a number of workers have isolated high coordination compounds of lanthanide(III) with Schiff bases [3-7]. Comparatively less is known about nine-coordinated compounds derived from lanthanide(III); thus it is worthwhile to study some nine-coordinated compounds. In the present work, we describe the nona-coordinated complexes of lanthanide(III) metals with 4-[N-(*p*-dimethylaminobenzalidene)amino] antipyrine semicarbazone (DABAAPS).

## EXPERIMENTAL

The lanthanide chlorides and nitrates (99.99%; pure grade) were obtained from Rare Earth Products Ltd. (India) and were used without further purification. The lanthanide isothiocyanates were prepared by adding a warm ethanolic solution of KNCS to a solution of lanthanide(III) nitrates. The  $\text{KNO}_3$  rapidly coagulated and the precipitated from the solution. The volume of the solution was reduced on a water bath, cooled, filtered and the filtrate was used for the complexation reaction [8].

The ligand 4-[N-(*p*-dimethylaminobenzalidene)amino]antipyrine semicarbazone was synthesized in the laboratory in two steps. In the first step, a solution of *p*-dimethylamine benzaldehyde (1 mmol) in absolute ethanol (20 mL) was mixed with 4-aminoantipyrine (1:1 mmol) in the same solvent (20 mL) and the reaction mixture was refluxed for 2-3 h. On cooling a yellow crystalline separated, which was filtered and dried in a desiccator over anhydrous  $\text{CaCl}_2$ . In the second step, the required semicarbazone was prepared by the following method by adding semicarbazone hydrochloride ( $\text{H}_2\text{N-NH-CO-NH}_2\cdot\text{HCl}$ ) (15 g) and 18 g of sodium acetate to 120 mL distilled water. The solution was mixed with 4-[N-(*p*-dimethylaminobenzalidene)-amino]antipyrine (prepared as above) in equimolar ratio in hot ethanol. The mixture was refluxed on a water bath for 1 h. On cooling a precipitate formed, which was filtered and washed with 50% ethanol. The product was crystallized from ethanol. The light yellow crystals were filtered and dried at 60 °C in an electric oven.

All the complexes were prepared by the following general method. The corresponding metal salts and the ligand in the required molar ratios were added to ethanol and reaction mixture was refluxed for 1-2 h. In each case the required solid product was obtained on cooling which was washed with the solvent and finally with diethyl ether and dried in *vacuo* over  $\text{P}_2\text{O}_5$  (yield ~70-75%).

The metal content was estimated as its oxide by direct combustion in a platinum crucible. The nitrogen was determined by the Kjeldahl method. The chloride content was determined by Volhard's method. The thiocyanate was determined by oxidizing it with bromine water to sulfate and subsequent precipitation as  $\text{BaSO}_4$ . The molecular weight of the complexes was determined cryoscopically in freezing nitrobenzene using a Beckmann thermometer of accuracy  $\pm 0.01$  °C. The conductivity measurements were carried out using a Toshniwal Conductivity Bridge (Type CL 01/01) and a dip type cell operated at 220 V AC mains. The magnetic measurements were carried out at room temperature on a Gouy balance and  $[\text{HgCo}(\text{SCN})_4]$  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 4000-200  $\text{cm}^{-1}$ . A Hilger Uvisvek spectrophotometer with a 1-cm quartz cell was employed for recording the visible spectra of  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Sm}^{3+}$  complexes. A thermogravimetric analysis of the lanthanide(III) complexes was carried out in static air, with open sample holders and a small platinum boat, at a heating rate of 6 °C  $\text{min}^{-1}$ .

## RESULTS AND DISCUSSION

The reaction of ethanolic solutions of lanthanide salts with 4-[N-(*p*-dimethylaminobenzalidene)-amino]antipyrine semicarbazone (DABAAPS) gave complexes of general composition  $\text{LnX}_3\cdot 2(\text{DABAAPS})$  ( $\text{Ln} = \text{La, Pr, Nd, Sm, Gd, Tb, Dy or Ho}$  and  $\text{X} = \text{Cl}^-$  or  $\text{NCS}^-$ ). The analytical data presented in Table 1 indicated that the complexes were pure and needed no further purification. The molar conductance values (Table 1) in  $\text{PhNO}_2$  of these complexes are

too low to account for any dissociation, therefore the complexes are considered to be non-electrolytes. The molecular weights of the complexes in  $\text{PhNO}_2$  are given in Table I along with values calculated on the basis of established formula of the complexes. The ratio of the molecular weight observed for  $\text{LnX}_3 \cdot 2(\text{DABAAPS})$  to that calculated is  $\sim 0.98$ , which shows that the complexes are monomeric in solution. The magnetic moment values of these complexes, determined at room temperature (Table 1), indicate that the La complexes are diamagnetic and the Pr, Nd, Sm, Gd, Tb, Dy and Ho complexes are paramagnetic. The values found are close to the theoretical values calculated using the formula  $\mu = g[J(J+1)]^{1/2}$  [9] and show little deviations from the Van Vleck values [10], indicating very little participation of the 4f-electrons in the bonding.

Table 1. Analytical, conductivity, molecular weight and magnetic moment data of lanthanide(III) complexes of DABAAPS.

Complex (empirical formula)	Analysis: found (calculated) %			$\Omega M$ ( $\text{ohm}^{-1} \text{cm}^2$ $\text{mole}^{-1}$ )	Exp. Mol. Wt. (formula wt.)	$\mu$ eff (B. M.)
	M	N	Anion			
$\text{LaCl}_3 \cdot 2(\text{DABAAPS})$	13.39 (13.52)	18.90 (19.07)	10.16 (10.36)	3.2	1021 (1027.5)	Diamagnetic
$\text{PrCl}_3 \cdot 2(\text{DABAAPS})$	13.46 (13.69)	18.86 (19.03)	10.12 (10.34)	2.9	1023 (1029.5)	3.60
$\text{NdCl}_3 \cdot 2(\text{DABAAPS})$	13.78 (13.94)	18.80 (18.98)	10.08 (10.31)	3.1	1027 (1032.5)	3.57
$\text{SmCl}_3 \cdot 2(\text{DABAAPS})$	14.21 (14.44)	18.70 (18.87)	10.04 (10.25)	2.8	1029 (1038.5)	1.65
$\text{GdCl}_3 \cdot 2(\text{DABAAPS})$	14.80 (15.01)	18.60 (18.74)	10.00 (10.18)	3.3	1038 (1045.5)	7.86
$\text{TbCl}_3 \cdot 2(\text{DABAAPS})$	14.97 (15.17)	18.52 (18.71)	9.98 (10.16)	3.2	1039 (1047.5)	9.28
$\text{DyCl}_3 \cdot 2(\text{DABAAPS})$	15.20 (15.46)	18.43 (18.64)	9.93 (10.13)	3.0	1043 (1051.0)	10.50
$\text{HoCl}_3 \cdot 2(\text{DABAAPS})$	15.36 (15.66)	22.38 (22.59)	9.91 (10.10)	2.9	1045 (1053.5)	10.33
$\text{La}(\text{NCS})_3 \cdot 2(\text{DABAAPS})$	12.47 (12.69)	21.59 (21.73)	15.69 (15.89)	3.3	1087 (1095.5)	Diamagnetic
$\text{Pr}(\text{NCS})_3 \cdot 2(\text{DABAAPS})$	12.62 (12.85)	21.47 (21.69)	15.67 (15.86)	3.1	1089 (1097.0)	3.41
$\text{Nd}(\text{NCS})_3 \cdot 2(\text{DABAAPS})$	12.80 (13.09)	21.40 (21.63)	15.68 (15.81)	3.4	1092 (1100)	3.53
$\text{Sm}(\text{NCS})_3 \cdot 2(\text{DABAAPS})$	13.30 (13.56)	21.30 (21.51)	15.55 (15.73)	3.5	1098 (1106)	1.60
$\text{Gd}(\text{NCS})_3 \cdot 2(\text{DABAAPS})$	13.81 (14.10)	21.20 (21.38)	15.46 (15.63)	3.4	1107 (1113)	7.81
$\text{Tb}(\text{NCS})_3 \cdot 2(\text{DABAAPS})$	14.02 (14.26)	21.18 (21.34)	15.45 (15.60)	3.3	1109 (1115)	9.43
$\text{Dy}(\text{NCS})_3 \cdot 2(\text{DABAAPS})$	14.27 (14.52)	21.10 (21.27)	15.40 (15.55)	4.1	1112 (1118.5)	10.61
$\text{Ho}(\text{NCS})_3 \cdot 2(\text{DABAAPS})$	14.42 (14.71)	21.08 (21.23)	15.38 (15.52)	3.6	1115 (1121)	10.43

*Infrared spectra.* The partial infrared data of the metal complexes are presented in Table 2. The  $\nu(\text{NH}_2)$  band of the hydrazinic nitrogen of semicarbazide ( $1622 \text{ cm}^{-1}$ ) is absent in the infrared spectra of the DABAAPS [11]. 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 [12]. The characteristic absorption of the carbonyl group in DABAAPS is observed at  $\sim 1705 \text{ cm}^{-1}$  [13]. In the complexes, this band is shifted toward lower energy in the  $1650\text{-}1640 \text{ cm}^{-1}$  region. The amide II band in DABAAPS has been observed at  $1570 \text{ cm}^{-1}$ . In all the present complexes this band is also shifted towards lower wave number by  $\sim 30 \text{ cm}^{-1}$ . This observation suggests coordination through the carbonyl oxygen atom. The strong band at  $\sim 1605 \text{ cm}^{-1}$  in DABAAPS apparently has a large contribution from the  $\nu(\text{C}=\text{N})$  mode of the semicarbazone moiety [14]. This has been observed as a blue shift in the position of the  $(\text{C}=\text{N})$  band in all the complexes as compared to the free ligand. Another strong band was observed at  $1620 \text{ cm}^{-1}$  due to the azomethine  $(\text{C}=\text{N})$  absorption. On complexation this band is shifted towards the lower frequency region, clearly indicating coordination through the azomethine-N atom [15, 16]. In the far infrared region the bands due to  $\nu(\text{Ln-N})$  and  $\nu(\text{Ln-O})$  are also observed [16, 17].

Table 2. Infrared absorption frequencies ( $\text{cm}^{-1}$ ) of lanthanide(III) complexes of DABAAPS.

Compounds	$\nu(\text{C}=\text{N})$ azomethini $\epsilon$	$\nu(\text{C}=\text{N})$ hydrazinic	$\nu(\text{C}=\text{O})$			$\nu(\text{Ln-O})/\nu(\text{Ln-N})$
			I	II	II	
DABAAPS	1620 s	1605s	1705 s	1570 s	1350 m	---
LaCl <sub>3</sub> .2(DABAAPS)	1595 s	1630 s	1645 s	1740 m	1335 m	480 m, 385 w
PrCl <sub>3</sub> .2(DABAAPS)	1600s	1635 s	1650 s	1542 m	1330 m	482 m, 378 w
NdCl <sub>3</sub> .2(DABAAPS)	1598 s	1638 s	1642 s	1545 m	1342 m	482 m, 390 w
SmCl <sub>3</sub> .2(DABAAPS)	1595 s	1635 s	1648 s	1540 m	1340 m	485 m, 382 w
GdCl <sub>3</sub> .2(DABAAPS)	1598 s	1632 s	1640 s	1545 m	1342 m	475 m, 375 w
TbCl <sub>3</sub> .2(DABAAPS)	1590 s	1635 s	1642 s	1549 m	1340 m	470 m, 370 w
DyCl <sub>3</sub> .2(DABAAPS)	1592 s	1635 s	1640 s	1540 m	1340 m	465 m, 365 m
HoCl <sub>3</sub> .2(DABAAPS)	1595 s	1638 s	1645 s	1542 m	1342 m	470 m, 360 m
La(NCS) <sub>3</sub> .2(DABAAPS)	1595 s	1637 s	1642 s	1547 m	1345 m	472 m, 362 m
Pr(NCS) <sub>3</sub> .2(DABAAPS)	1592 s	1635 s	1642 s	1545 m	1342 m	480 m, 382 w
Nd(NCS) <sub>3</sub> .2(DABAAPS)	1590 s	1632 s	1640 s	1540 m	1344 m	478 m, 375 w
Sm(NCS) <sub>3</sub> .2(DABAAPS)	1592 s	1635 s	1645 s	1542 m	1340 m	462 m, 380 w
Gd(NCS) <sub>3</sub> .2(DABAAPS)	1595 s	1638 s	1648 s	1545 m	1342 m	470 m, 370 w
Tb(NCS) <sub>3</sub> .2(DABAAPS)	1598 s	1637 s	1642 s	1540 m	1345 m	472 m, 372 w
Dy(NCS) <sub>3</sub> .2(DABAAPS)	1590 s	1635 s	1640 s	1542 m	1342 m	475 m, 386 w
Ho(NCS) <sub>3</sub> .2(DABAAPS)	1595 s	1630 s	1642 s	1545 m	1340 m	472 w, 382 w

In the past various workers [18, 19] were interested in investigating the mode of bonding of NCS<sup>-</sup> in various metal-complex compounds. In the present complexes the infrared absorption frequencies due to  $\nu(\text{C-N})$  ( $\nu_1$ ),  $\nu(\text{C-S})$  ( $\nu_3$ ) and  $\delta(\text{N-C-S})$  ( $\nu_2$ ) are identified at  $\sim 2040$ ,  $845$  and  $470 \text{ cm}^{-1}$  respectively. These frequencies are associated with the terminal N-bonded isothiocyanate ion [19]. The  $\nu(\text{Ln-Cl})$  in the chloro complexes was detected at  $\sim 230 \text{ cm}^{-1}$ .

*Electronic spectra.* The electronic spectra of the complexes (Table 3) showed a shift in the band position towards the lower wave numbers as compared to those of the metal salts. The bands observed in the case of Pr<sup>3+</sup>, Nd<sup>3+</sup> and Sm<sup>3+</sup> complexes could be assigned to the transitions from <sup>3</sup>H<sub>4</sub>, <sup>4</sup>I<sub>9/2</sub> and <sup>4</sup>F<sub>3/2</sub> (ground levels) to the excited J-levels of the respective 4f<sup>6</sup> configurations. The

present data also show that the nephelauxetic values for different J-levels vary considerably. The  $(1-\beta)$  values were used to estimate Sinha's covalency parameter ( $\delta\%$ ) [20]. Another bonding parameter  $b^{1/2}$ , which measures the amount of 4f orbital-ligand-orbital mixing in these compounds and the covalency angular overlap parameter ( $\eta$ ) were also calculated. The values of  $(1-\beta)$ ,  $b^{1/2}$ ,  $\delta\%$  and  $\eta$  at corresponding transitions are also included in Table 3. The positive values for  $(1-\beta)$  and  $\delta\%$  in these coordination compounds suggests that the bonding between the metal and the ligand is covalent compared with the bonding between the metal and an aquo ion. The values of the bonding parameter ( $b^{1/2}$ ) and angular overlap parameter ( $\eta$ ) were found to be positive indicating covalent bonding [21].

Table 3. Electronic spectral data ( $\text{cm}^{-1}$ ) and related bonding parameters of lanthanide(III) isothiocyanato complexes of DABAAPS.

Complexes	Ln(NCS) <sub>3</sub> electronic spectral bands	Complex electronic spectral bands	Energy levels	(1-β)	β	$b^{1/2}$	δ%	η
Pr (NCS) <sub>3</sub> .2(DABAAPS)	22400	22250	$^3H_4 \rightarrow ^3P_2$	0.00669	0.99330	0.04089	0.67351	0.00710
	21230	21050	$\rightarrow ^3P_1$	0.00847	0.99152	0.04601	0.85424	0.00426
	20800	20620	$\rightarrow ^3P_0$	0.00865	0.99134	0.04650	0.87255	0.00435
	16900	16720	$\rightarrow ^1D_2$	0.01065	0.98934	0.05159	1.07647	0.00534
Nd(NCS) <sub>3</sub> .2(DABAAPS)	19400	19200	$^4I_{1/2} \rightarrow ^2G_{7/2}$	0.01030	0.98969	0.05074	1.04072	0.00519
	17400	17200	$\rightarrow ^4G_{5/2}, ^4G_{7/2}$	0.01149	0.98850	0.05359	1.16236	0.00580
	13400	13240	$\rightarrow ^2S_{1/2}, ^4F_{3/2}$	0.01194	0.98805	0.05463	1.20844	0.00602
	12500	12240	$\rightarrow ^4F_{5/2}, ^4H_{9/2}$	0.02080	0.97920	0.07211	2.11418	0.01056
Sm(NCS) <sub>3</sub> .2(DABAAPS)	24900	24700	$^4H_{5/2} \rightarrow ^4F_{3/2}$	0.00803	0.99196	0.04480	0.80950	0.00404
	24000	23820	$\rightarrow ^6P_{3/2}$	0.00750	0.99250	0.04330	0.75566	0.00377
	21600	21440	$\rightarrow ^4I_{1/2}$	0.00740	0.99260	0.04301	0.74552	0.00372

**Thermal studies.** The thermal studies (thermogravimetric analysis) indicate that all the lanthanide(III) chloride complexes are stable up to 215 °C, which shows that there are no coordinated or uncoordinated water molecules in these complexes. The complexes underwent a two-stage decomposition between 250-410 °C due to the organic moiety and between 425-740 °C due to the formation of lanthanide oxides [22, 23].

**Stereochemistry of the complexes.** Coordination numbers of the lanthanide ions normally vary between 6 and 10, but are often higher with small bidentate ligands. In the present complexes [Ln(DABAAPS)<sub>2</sub>X<sub>3</sub>] (X = Cl<sup>-</sup> or NCS<sup>-</sup>) the electrolytic conductivity data indicate that all the coordinating anions are present in the coordination sphere. The infrared spectral studies suggest that DABAAPS behave as tridentate (N,N,O) ligand. Thus we conclude that the coordination number of central metal ion is nine in these complexes [1] with the ligand acting as a tri-coordinate lying through two-N and one-O atoms. This is consistent with the data obtained from the elemental analyses.

## REFERENCES

- Koppikar, D.K.; Sivapulliah, P.V.; Ramakrishnan, L.; Soundararajan, S. *Struct. Bonding* **1967**, 34, 135.
- Clearfield, Abraham; Gopal, Ramanathan; Oslen, Radley H. *Inorg. Chem.* **1977**, 16, 911.

3. Dutta, R.L.; Das, B.R. *J. Scient. Ind. Res.* **1988**, *47*, 547.
4. Agarwal, R.K.; Sarin, R.K.; Prasad, Ram *Polish J. Chem.* **1993**, *67*, 1947.
5. Agarwal, R.K.; Sarin, R.K. *Polish J. Chem.* **1993**, *67*, 1925.
6. Agarwal, R.K.; Sarin, R.K. *Polyhedron* **1993**, *12*, 2411.
7. Agarwal, R.K.; Sarin, R.K. *Synth. React. Inorg. Met.-Org. Chem.* **1994**, *24*, 185.
8. Cousin, D.R.; Hart, F.A. *J. Inorg. Nucl. Chem.* **1968**, *30*, 3009.
9. Selwood, P.W. *Magneto-Chemistry*, Interscience: New York; **1960**.
10. Van Vleck, J.H.; Frandk, N. *Phys. Rev.* **1929**, *34*, 1494.
11. Reed G.; Cohn, M. *J. Biol. Chem.* **1970**, *255*, 662.
12. Levanon, H. *J. Chem. Phys.* **1968**, *49*, 2031.
13. Campbell, M.J.; Grzeskowick, R. *J. Inorg. Nucl. Chem.* **1968**, *30*, 1865.
14. Dyer, J.F. *Application of Absorption Spectroscopy of Organic Compounds*, Prentice-Hall: New Delhi; **1984**.
15. Agarwal, R.K.; Arora, K. *Polish J. Chem.* **1993**, *67*, 219.
16. Radhakrishnan, P.K.; Indrasenan, P.; Nair, C.G.R. *Polyhedron* **1984**, *3*, 67.
17. Radhakrishnan, P.K.; Indrasenan, P. *J. Indian Chem. Soc.* **1990**, *67*, 243.
18. Burmeister, J.L. *Coord. Chem. Rev.* **1966**, *1*, 205; **1968**, *3*, 225.
19. Bailly, R.A.; Kozak, S.L.; Michelson, T.W.; Mills, W.N. *Coord. Chem. Rev.* **1971**, *6*, 407.
20. Sinha, S.P. *J. Inorg. Nucl. Chem.* **1971**, *33*, 2205.
21. Mohan, J.; Tandon, J.P.; Gupta, N.S. *Inorg. Chim. Acta* **1986**, *111*, 187.
22. Agarwal, R.K.; Gupta, S.K. *Thermochim. Acta* **1986**, *99*, 357.
23. Agarwal, R.K.; Gupta, S.K. *Polish J. Chem.* **1987**, *61*, 341.