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# Anionic Effect on Lanthanide(III) Metal Coordination Compounds of 4[N-(Benzalidene) Amino] Antipyrine Semicarbazone

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In the present work, the authors have studied the effect of chloro and perchlorato as anionic ligand on lanthanide(III) coordination compounds of 4[N-(benzalidene) amino] antipyrine semicarbazone. The isolated compounds have the composition $LnCl_3 \cdot 2(BAAPS)$ and $Ln(ClO_4)_3 \cdot 2(BAAPS)$ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho). The compounds were characterized by elemental analysis, molar conductance, molecular weight, magnetic susceptibility, infra red and electronic spectra. The coordination number of central metal ion is either six or nine depending on the nature of anionic ligand. Thermal properties of the compounds were also studied.

**Key Words: Lanthanide, Coordination compounds, Semicarbazone.**

## INTRODUCTION

Lanthanide ions with their 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]. In the present work, we describe some six- and nine-coordinated complexes of lanthanide(III) with 4[N-(benzalidene) amino] antipyrine semicarbazone (BAAPS). The coordinating ability of this ligand with lanthanide(III) nitrates was already investigated by Agarwal *et al.*[2].

## EXPERIMENTAL

The lanthanide chlorides and oxides were obtained from Rare Earth Products Ltd. (India). The lanthanide perchlorates were prepared by heating the corresponding oxides with perchloric acid and evaporating off the excess of acid[3]. The ligand BAAPS was prepared by known method[2].

All the complexes were synthesized by the following methods:

**$LnCl_3 \cdot 2(BAAPS)$:** A methanolic solution of the ligand was refluxed for 1 h and then a methanolic solution of the trivalent methanolic chloride was added in required molar ratio. The reaction mixture was refluxed for *ca.* 2 h and then kept

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for a slow heating on the hot plate till a thick layer of precipitate settled. The supernatant liquid was decanted off and the product was dried. It was then washed several times with methanol to remove any excess of the metal chloride and/or ligand. Finally it was washed with anhydrous diethyl-ether and dried *in vacuo* over $P_4O_{10}$.

**$Ln(ClO_4)_3 \cdot 2(BAAPS)$:** The solutions of lanthanide(III) perchlorate (1 mmol) and BAAPS (2.1 mmol) in hot methanol (15 mL each) were mixed and refluxed on a steam bath for 2 h. It was then concentrated to about 10 mL and diethyl-ether (20 mL) was added with constant stirring to separate the desired compound, which was collected and washed with diethyl-ether. All the compounds were dried under vacuum over $P_4O_{10}$.

All the physico-chemical measurements were performed by reported method[2].

## RESULTS AND DISCUSSION

The reaction of a non-aqueous solution of lanthanide(III) salts with BAAPS resulting in complexes of the general composition $LnX_3 \cdot 2(BAAPS)$ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho; X = Cl or $ClO_4$). The analytical data of the present complexes are presented in Table-1. The complexes are fairly stable and could be stored for a long time and are non-hygroscopic in nature. The complexes do not possess sharp melting points and decompose at higher temperatures. The molar conductance values (Table-1) of $LnCl_3 \cdot 2(BAAPS)$ are too low to account for any dissociation; therefore the complexes are non-electrolytes. The perchlorato complexes behave as 1 : 3 electrolytes in $PhNO_2$ suggesting all the perchlorato groups are present outside the coordination sphere[4]. Data on the molecular weights of the complexes in $PhNO_2$ are given in Table-1. The ratio of molecular weight observed for $LnCl_3 \cdot 2(BAAPS)$ to that of calculated is *ca.* 0.98 which shows that the complexes are monomeric in nature. In case of $Ln(ClO_4)_3 \cdot 2(BAAPS)$, the ratio is found to be approximately 0.25. This data further supports that 4 species are formed in perchlorato complexes.

The magnetic moment values observed in the present study are presented in Table-1, which shows that lanthanum complexes are diamagnetic in nature. All other tripositive lanthanide ions are paramagnetic in nature due to the presence of 4f-electrons, which are effectively shielded by $5s^25p^6$ electrons[5, 6].

The partial infrared spectral bands of BAAPS and its lanthanide(III) coordination compounds are presented in Table-2. The characteristic absorption of the carbonyl group in BAAPS is observed[7] at 1700 $cm^{-1}$. In all the complexes studied herein, this band is shifted towards lower energy in the 1650–1640 $cm^{-1}$ region. The amide-II band in the free ligand has been observed at 1565 $cm^{-1}$. In all the present complexes, this band is also shifted towards lower wave numbers by *ca.* 30 $cm^{-1}$. This observation suggests coordination through the carbonyl oxygen atom. The strong band at 1600 $cm^{-1}$ in BAAPS apparently has a large contribution from the $\nu(C{=}N)$ mode of semicarbazone moiety[8]. This has been observed as a blue shift in the position of the (C=N) band in all complexes as compared to the free ligand. Another strong band was observed at 1610 $cm^{-1}$ due to azomethinic (C=N) absorption. On complexation this band is shifted towards the lower frequency region, clearly indicating the coordination through the azomethinic N-atom[9, 10]. In far infrared region the bands due to $\nu$(Ln—N)/$\nu$(Ln—O) are also observed[11, 12].

TABLE-1
ANALYTICAL, CONDUCTIVITY, MOLECULAR WEIGHT AND MAGNETIC MOMENT DATA OF LANTHANIDE(III) COORDINATION COMPOUNDS OF BAAPS

| Complex | Analysis (%), found (calcd.) | | | $\Lambda_m$ (ohm$^{-1}$ cm$^2$ mole$^{-1}$) | m.w. found (calcd.) | $\mu_{eff}$ (B.M.) |
|---|---|---|---|---|---|---|
| | Ln | N | Anion | | | |
| $LaCl_3 \cdot 2(BAAPS)$ | 14.63 | 17.70 | 11.20 | 2.1 | 938 | Diamag. |
| | (1476) | (17.84) | (11.31) | | (941.5) | |
| $PrCl_3 \cdot 2(BAAPS)$ | 14.80 | 17.68 | 11.19 | 1.9 | 940 | 3.41 |
| | (14.94) | (17.80) | (11.28) | | (943.5) | |
| $NdCl_3 \cdot 2(BAAPS)$ | 15.10 | 17.62 | 11.16 | 1.8 | 942 | 3.52 |
| | (15.21) | (17.74) | (11.25) | | (946.5) | |
| $SmCl_3 \cdot 2(BAAPS)$ | 15.63 | 17.50 | 11.09 | 2.2 | 948 | 1.60 |
| | (15.74) | (17.63) | (11.18) | | (952.5) | |
| $GdCl_3 \cdot 2(BAAPS)$ | 16.26 | 17.37 | 10.99 | 1.8 | 954 | 7.80 |
| | (1636) | (17.50) | (11.09) | | (959.5) | |
| $TbCl_3 \cdot 2(BAAPS)$ | 16.42 | 17.33 | 10.96 | 2.3 | 957 | 9.47 |
| | (16.53) | (17.47) | (11.07) | | (961.5) | |
| $DyCl_3 \cdot 2(BAAPS)$ | 16.71 | 17.28 | 10.91 | 2.1 | 961 | 10.59 |
| | (16.83) | (17.40) | (11.03) | | (965) | |
| $HoCl_3 \cdot 2(BAAPS)$ | 16.97 | 17.22 | 10.87 | 2.2 | 963 | 10.53 |
| | (17.05) | (17.36) | (11.00) | | (967.5) | |
| $La(ClO_4)_3 \cdot 2(BAAPS)$ | 12.19 | 14.69 | 26.09 | 78.9 | 286 | Diamag. |
| | (12.26) | (14.82) | (26.33) | | (1133.5) | |
| $Pr(ClO_4)_3 \cdot 2(BAAPS)$ | 12.32 | 14.67 | 26.01 | 80.3 | 287 | 3.58 |
| | (12.41) | (14.79) | (26.28) | | (1135.5) | |
| $Nd(ClO_4)_3 \cdot 2(BAAPS)$ | 12.54 | 14.63 | 25.98 | 82.1 | 287.5 | 3.56 |
| | (12.64) | (14.75) | (26.21) | | (1138.5) | |
| $Sm(ClO_4)_3 \cdot 2(BAAPS)$ | 12.99 | 14.53 | 25.93 | 79.3 | 289 | 1.58 |
| | (13.10) | (14.67) | (26.08) | | (1144.5) | |
| $Gd(ClO_4)_3 \cdot 2(BAAPS)$ | 13.50 | 14.44 | 25.78 | 81.9 | 290 | 7.80 |
| | (13.63) | (14.58) | (25.92) | | (1151.5) | |
| $Tb(ClO_4)_3 \cdot 2(BAAPS)$ | 13.64 | 14.42 | 25.69 | 82.1 | 292 | 9.81 |
| | (13.78) | (14.56) | (25.87) | | (1153.5) | |
| $Dy(ClO_4)_3 \cdot 2(BAAPS)$ | 13.93 | 14.39 | 25.59 | 80.9 | 293 | 10.34 |
| | (14.04) | (14.52) | (25.79) | | (1157) | |
| $Ho(ClO_4)_3 \cdot 2(BAAPS)$ | 14.10 | 14.36 | 25.53 | 80.7 | 294 | 10.51 |
| | (14.23) | (14.48) | (25.74) | | (1159.5) | |

### TABLE-2
### INFRARED ABSORPTION FREQUENCIES (cm$^{-1}$) OF LANTHANIDE(III) COORDINATION COMPOUNDS OF BAAPS

| Assignments | $\nu$(C=N) (azomethine) | $\nu$(C=N) (hydrazinic) | $\nu$(C=O) | | | $\nu$(Ln—N), $\nu$(Ln—O) |
|---|---|---|---|---|---|---|
| | | | I | II | III | |
| BAAPS | 1610 s | 1600 s | 1700 s | 1565 m | 1350 m | — |
| LaCl$_3$·2(BAAPS) | 1590 s | 1622 s | 1645 s | 1535 m | 1335 m | 430 m,<br>390 w |
| PrCl$_3$·2(BAAPS) | 1588 s | 1630 s | 1650 s | 1530 m | 1332 m | 425 m,<br>375 w |
| NdCl$_3$·2(BAAPS) | 1585 s | 1625 s | 1652 s | 1532 m | 1335 m | 432 m,<br>370 w |
| SmCl$_3$·2(BAAPS) | 1580 s | 1632 s | 1645 s | 1530 m | 1330 m | 422 m,<br>365 w |
| GdCl$_3$·2(BAAPS) | 1585 s | 1630 s | 1640 s | 1528 m | 1332 m | 425 m,<br>368 w |
| TbCl$_3$·2(BAAPS) | 1582 s | 1625 s | 1642 s | 1532 m | 1330 m | 422 m,<br>370 w |
| DyCl$_3$·2(BAAPS) | 1585 s | 1630 s | 1645 s | 1535 m | 1325 m | 370 m,<br>372 w |
| HoCl$_3$·2(BAAPS) | 1582 s | 1625 s | 1640 s | 1530 m | 1332 m | 422 m,<br>368 w |
| La(ClO$_4$)$_3$·2(BAAPS) | 1592 s | 1620 s | 1652 | 1535 m | 1335 m | 430 m,<br>375 w |
| Pr(ClO$_4$)$_3$·2(BAAPS) | 1590 s | 1625 s | 1645 s | 1530 m | 1332 m | 425 m,<br>378 w |
| Nd(ClO$_4$)$_3$·2(BAAPS) | 1585 s | 1630 s | 1640 s | 1535 m | 1330 m | 422 m,<br>375 w |
| Sm(ClO$_4$)$_3$·2(BAAPS) | 1592 s | 1632 s | 1645 s | 1530 m | 1332 m | 435 m,<br>368 w |
| Gd(ClO$_4$)$_3$·2(BAAPS) | 1590 s | 1625 s | 1650 s | 1528 m | 1330 m | 432 m,<br>365 w |
| Tb(ClO$_4$)$_3$·2(BAAPS) | 1582 s | 1630 s | 1645 s | 1532 m | 1328 m | 435 m,<br>370 w |
| Dy(ClO$_4$)$_3$·2(BAAPS) | 1592 s | 1625 s | 1642 s | 1525 m | 1325 m | 430 m,<br>365 w |
| Ho(ClO$_4$)$_3$·2(BAAPS) | 1595 s | 1628 s | 1645 s | 1532 m | 1330 m | 432 m,<br>370 w |

In all the perchlorato complexes, only two strong $\nu_3$ and $\nu_4$ bands are observed at 1115–1090 cm$^{-1}$ and 640–620 cm$^{-1}$ regions respectively for perchlorate ion indicating that tetrahedral symmetry has not been disturbed on complexation and the perchlorate ions are not bonded to metal ion[13, 14]. This conclusion is also supported by conductance and molecular weight data.

Lanthanum(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 $^3H_4$, $^4I_{9/2}$, $^6H_{5/2}$, $^8S_{7/2}$ and $^6H_{15/2}$ 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 evidence of a higher degree of covalency than existing in the aquo ligands[15, 16]. 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 ($\beta$) in these compounds. From the $\beta$-values the covalence factor (b$^{1/2}$), Sinha parameter ($\delta$%) and the covalency angular overlap parameter ($\eta$) have been calculated (Table-3). The positive values for $(1 - \beta)$ and $\delta$% in these coordination compounds suggested 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 parameter of bonding (b$^{1/2)}$ and angular overlap parameter ($\eta$) were found to be positive, indicating covalent bonding.

TABLE-3
ELECTRONIC SPECTRAL DATA (cm$^{-1}$) AND RELATED BONDING PARAMETERS OF $LnCl_3 \cdot 2$(BAAPS)

| Complex | $LnCl_3$ electronic spectral bands | Complex electronic spectral bands | J-levels | $\beta$ | b$^{1/2}$ | $\delta$ (%) | $\eta$ |
|---|---|---|---|---|---|---|---|
| $PrCl_3 \cdot 2$(BAAPS) | 22470 | 22300 | $^3H_4 \rightarrow {}^3P_2$ | 0.9964 | 0.0298 | 0.3572 | 0.0019 |
| | 21325 | 21230 | $\rightarrow {}^3P_2$ | 0.9955 | 0.0333 | 0.4470 | 0.0023 |
| | 20750 | 20620 | $\rightarrow {}^3P_0$ | 0.9937 | 0.0395 | 0.6299 | 0.0032 |
| | 17000 | 16880 | $\rightarrow {}^1D_2$ | 0.9929 | 0.0419 | 0.7100 | 0.0036 |
| $NdCl_3 \cdot 2$(BAAPS) | 19550 | 19480 | $^4I_{9/2} \rightarrow {}^2G_{9/2}$ | 0.9964 | 0.0299 | 0.3592 | 0.0019 |
| | 17360 | 17260 | $\rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ | 0.9942 | 0.0379 | 0.5793 | 0.0030 |
| | 13360 | 13630 | $\rightarrow {}^2S_{3/2}, {}^4F_{7/2}$ | 0.9978 | 0.0234 | 0.2194 | 0.0012 |
| | 12470 | 12430 | $\rightarrow {}^4F_{3/2}, {}^4H_{9/2}$ | 0.9967 | 0.0283 | 0.3210 | 0.0017 |
| $SmCl_3 \cdot 2$(BAAPS) | 24870 | 24830 | $^4H_{5/2} \rightarrow {}^4F_{9/2}$ | 0.9983 | 0.0200 | 0.1602 | 0.0009 |
| | 24000 | 23835 | $\rightarrow {}^6P_{5/2}$ | 0.9931 | 0.0414 | 0.6917 | 0.0035 |
| | 21550 | 21520 | $\rightarrow {}^4I_{13/2}$ | 0.9986 | 0.0186 | 0.1391 | 0.0008 |

Thermoanalytical results of [Ln(BAAPS)$_2$Cl$_3$] (Ln = La, Gd or Dy) suggest that these complexes do not show the presence of water molecule either in or out of the coordination sphere. The analysis of the thermal curves suggests that above 210°C the compounds start to lose mass with partial evaporation of the organic ligand up to a temperature of 290°C; the mass loss corresponds to one molecule of BAAPS and in the temperature range 320–400°C, another molecule of BAAPS is also lost. The residues obtained after heating up to 825°C, to constant weight, are very close to that expected for the lanthanide oxides[17].

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