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# STUDIES OF COMPLEXES OF LANTHANIDE(III) WITH BENZOIN

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**Abstract**—Eight lanthanide complexes of the type $[LnB_2Cl_3] \cdot nH_2O$ (Ln = La, Pr, Sm, Tb, Ho, $n = 2$; Eu, $n = 1$; Nd, $n = 4$; Dy, $n = 3$; and B = benzoin) have been synthesized and characterized by chemical analysis, molar conductance, IR, electronic, resonance Raman, fluorescence, $^1$H NMR and X-ray photoelectron spectroscopies and TG–DTA analysis.

The solution behaviour of $La^{III}$ and $Ce^{III}$ with benzoin in acetone has been studied,[1] but no paper has so far reported on the synthesis of solid complexes of lanthanide(III) with benzoin. It was therefore of interest to investigate the solid lanthanide complexes of benzoin. The work described here is an attempt in that direction and deals with the synthesis of lanthanide metal complexes of benzoin and the characterization of the bonding model by physical methods.

## EXPERIMENTAL

### *Methods and materials*

Benzoin was purchased from Ger, A. G. Lanthanide chlorides were made from their oxides and hydrochloric acid. All other reactants were of high purity and were used as purchased without any further purification.

Chemical analyses for carbon, hydrogen and chlorine, both for the ligands and the complexes, were carried out on a Perkin–Elmer 240c Elemental Analyser. Lanthanide metals were determined volumetrically by EDTA titration[2] using xylenol orange as the indicator. Molar conductance in dimethylsulphoxide (DMSO) at 0.001 mol dm$^{-3}$ concentration was measured with a DDS-II A molar conductometer at 298 K. Electronic spectra were recorded in a Shimadzu UV-240 double beam spectrophotometer using fresh absolute methanol solutions of the sample. IR spectra were recorded in the 4000–200 cm$^{-1}$ range on a NIC-5DX instrument (CsI pellets). Resonance Raman (RR) spectra were recorded on a Nicolet Raman 910 apparatus. X-ray photoelectron spectra (XPS) were taken on a PHI-550 apparatus; non-monochromatic Mg-$K_\alpha$ radiation was used from an X-ray gun operated at 15 kV and 20 mA under a pressure of $10^{-9}$ mbar using the carbon 1*s* peak at 284.6 eV as standard. Thermogravimetric (TG) and differential scanning calorimetry (DSC) curves were recorded on a Dupont 1090 system between room temperature and 800°C. TG diagrams were recorded in a dynamic atmosphere of highly pure nitrogen (5 ml min$^{-1}$) at a heating rate of 10°C min$^{-1}$. DSC curves were obtained in a static atmosphere of nitrogen at the same heating rate as for the TG curves.

### *Preparation of the complexes*

All complexes were obtained following a similar method. The lanthanide(III) chloride ethanol solution was slowly added to an ethanol solution of benzoin with a metal salt to ligand molar ratio of Ln: benzoin = 1:2 and refluxed for 2 h, then concentrated to a small volume and the product precipitated. It was then filtered off, washed with cooled EtOH followed by $Et_2O$ and dried *in vacuo*. The results from the chemical analysis for the complexes prepared are summarized in Table 1.

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Table 1. Physical properties and analytical data of the complexes

| Complex | Dec. temp. (°C) | Found (Calc.), % | | | | $\Lambda_{M_C}$ [a] |
|---|---|---|---|---|---|---|
| | | | H | Cl | Ln | |
| $[LaB_2Cl_3] \cdot 2H_2O$ | 178 | 47.7 (47.6) | 3.9 (4.0) | 15.0 (15.1) | 18.0 (19.7) | 4.1 |
| $[PrB_2Cl_3] \cdot 2H_2O$ | 164 | 48.0 (47.5) | 4.2 (4.0) | 15.1 (15.0) | 19.7 (19.9) | 3.0 |
| $[NdB_2Cl_3] \cdot 4H_2O$ | 162 | 45.0 (45.2) | 4.3 (4.1) | 14.2 (14.3) | 19.2 (19.3) | 2.9 |
| $[SmB_2Cl_3] \cdot 2H_2O$ | 163 | 46.6 (46.9) | 4.0 (3.9) | 14.8 (14.9) | 20.9 (21.0) | 1.2 |
| $[EuB_2Cl_3] \cdot H_2O$ | 168 | 47.8 (48.0) | 4.1 (3.7) | 15.1 (15.2) | 21.6 (21.7) | 1.0 |
| $[TbB_2Cl_3] \cdot 2H_2O$ | 171 | 46.2 (46.3) | 4.0 (3.9) | 14.7 (14.7) | 21.8 (21.9) | 4.3 |
| $[DyB_2Cl_3] \cdot 3H_2O$ | 162 | 45.3 (45.0) | 3.9 (4.1) | 14.2 (14.4) | 21.8 (21.7) | 1.5 |
| $[HoB_2Cl_3] \cdot 2H_2O$ | 166 | 45.9 (46.0) | 3.9 (3.9) | 14.5 (14.6) | 22.5 (22.5) | 0.8 |

[a] S cm$^2$ mol$^{-1}$ and *ca* $10^{-3}$ M DMSO.

## RESULTS AND DISCUSSION

Elemental analyses, IR and XPS data and the molecular weight determination by Rast's method indicate that the complexes were in a mononuclear form and possess the general formula $[LnB_2Cl_3] \cdot nH_2O$ (B = benzoin). They are air-stable solids with the colour of the corresponding lanthanide(III) ion, soluble in methanol, ethanol, acetone, dimethylformamide and DMSO, but insoluble in water and benzene. The molar conductances of the complexes fall in the range expected for non-electrolytes[3] and show little solvolytic tendency in DMSO.

### *IR and RR spectra*

The important bands observed in the IR and RR spectra of the ligand and the complexes are summarized in Table 2, along with their assignments. The broad band between 3414 and 3377 cm$^{-1}$ due to the stretching modes of $\nu$(O—H) of the ligand are shifted downfield to 3380–3160 cm$^{-1}$ in the complexes, which arises from the overlapping of the hydroxyl group and the water molecules, and the fact that the stretching modes of $\nu$(C—OH) in the complexes are shifted *ca* 10 cm$^{-1}$ to lower wavenumbers than in the ligand. This indicates that the hydroxyl group of the ligand binds to lan-

Table 2. Significant IR and RR bands of the ligand and its complexes (cm$^{-1}$)

| Compound | IR | | | | | RR | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $\nu$(OH) | $\nu$(C=O) | $\nu$(C—O) | $\nu$(Ln—O) | $\nu$(Ln—Cl) | $\nu$(OH) | $\nu$(C=O) | $\nu$(C—O) | $\nu$(Ln—O) | $\nu$(Ln—Cl) |
| Benzoin (B) | 3414 | 1680 | 1092 | | | 3070 | 1680 | 1104 | | |
| | 3377 | | | | | 3052 | | | | |
| $[LaB_2Cl_3] \cdot 2H_2O$ | 3354 | 1648 | 1082 | 470 | 290 | 3080 | 1648 | 1082 | 446 | 264 |
| | 3158 | | | | | 3050 | | | | |
| $[PrB_2Cl_3] \cdot 2H_2O$ | 3354 | 1647 | 1082 | 462 | 268 | 3072 | 1648 | 1072 | 440 | 584 |
| | 3157 | | | | | 3048 | | | | |
| $[NdB_2Cl_3] \cdot 4H_2O$ | 3328 | 1649 | 1080 | 458 | 265 | 3076 | 1647 | 1076 | 442 | 252 |
| | 3169 | | | | | 3047 | | | | |
| $[SmB_2Cl_3] \cdot 2H_2O$ | 3329 | 1647 | 1080 | 460 | 269 | 3079 | 1648 | 1069 | 443 | 248 |
| | 3169 | | | | | 3047 | | | | |
| $[EuB_2Cl_3] \cdot H_2O$ | 3343 | 1649 | 1082 | 458 | 268 | 3078 | 1648 | 1078 | 442 | 248 |
| | 3184 | | | | | 3052 | | | | |
| $[TbB_2Cl_3] \cdot 2H_2O$ | 3382 | 1649 | 1082 | 451 | 268 | 3074 | 1646 | 1080 | 441 | 246 |
| | 3188 | | | | | 3050 | | | | |
| $[DyB_2Cl_3] \cdot 3H_2O$ | 3312 | 1649 | 1082 | 451 | 267 | 3072 | 1644 | 1078 | 441 | 247 |
| | 3200 | | | | | 3051 | | | | |
| $[HoB_2Cl_3] \cdot 2H_2O$ | 3340 | 1646 | 1080 | 450 | 266 | 3071 | 1646 | 1078 | 440 | 247 |
| | 3190 | | | | | 3050 | | | | |

thanide ion.[4] The most informative and intense bands due to the ketonic carbonyl group are recorded at 1680 cm$^{-1}$ in the ligand and are shifted to much lower frequencies at *ca* 1648 cm$^{-1}$ in the complexes, which demonstrates the coordination of the ketonic oxygen to lanthanide ion.[5] The several new bands observed in the far-IR spectra at 470–450 and 290–265 cm$^{-1}$ are tentatively assigned to Ln—O and Ln—Cl stretching modes, respectively. All the complexes exhibit an intense broad band in the water stretching region and a shoulder in the water bending region, which suggest that water molecules in the complexes are in uncoordinated form. On the basis of the discussion referred to above, it is possible to conclude that the ligand is attached to the metal ion by oxygen involving hydroxyl and ketonic groups, and seven-coordinated complexes are formed.

The RR spectra of the ligand and the complexes are similar to the IR spectra (Table 2). No new bands are observed in the RR spectra which contact with the coordination geometry related to the corresponding IR spectra, indicating that the complexes are asymmetric.[6,7]

### *Electronic spectra*

The electronic spectra of Nd$^{III}$, Sm$^{III}$, Dy$^{III}$ and Ho$^{III}$ complexes were recorded in $1 \times 10^{-3}$ mol dm$^{-3}$ absolute MeOH solutions. The spectra of the complexes show a shift of the bands towards lower energy as compared to those of the aquo ions[8] due to the nephelauxetic effect. The band shape of hypersensitive transition is similar in both the solid (Nujol) and solution (MeOH) phases, which clearly indicates that the complexes retain the same coordination number. The bonding parameter ($b^{1/2}$), the covalency parameter ($\delta$) and nephelauxetic ratio ($\bar{\beta}$) have been calculated[9,10] and are compiled in Table 3. The nephelauxetic parameter ($\bar{\beta}$) is less than unity, while the bonding parameter ($b^{1/2}$) and Sinha's parameter ($\delta$) are positive, indicating a moderate covalent character of the bond between the metals and ligands.[11]

### $^1$H *NMR spectra*

The $^1$H NMR spectrum of benzoin displays signals at 6.08, 6.04 and 7.10–8.01 ppm, assignable to —OH, —CH— and aromatic protons, respectively. The observed downfield shifts of the —OH and —CH— signals to *ca* 6.01 and 5.98 ppm in the spectra of the complexes are indicative of involvement in coordination of ketonic and hydroxylic oxygen, respectively. Furthermore, the presence of a small downfield shift in the aromatic proton signals confirms the bonding formation.

Table 3. Electronic spectra of Nd$^{III}$, Sm$^{III}$, Dy$^{III}$ and Ho$^{III}$ complexes[a]

| | $\lambda_{max}$(cm$^{-1}$) | | | Calculated spectral parameters | | |
|---|---|---|---|---|---|---|
| Compound | Solid | Solution ($\varepsilon$) | Assignment | $\bar{\beta}$ | $b^{1/2}$ | $\delta$ |
| Benzoin (B) | 38,760, 48,078 | 41,322, 47,170<br>(3.3, 2.1) | | | | |
| [NdB$_2$Cl$_3$]·4H$_2$O | 39,700, 48,209 | 41,200, 47,486<br>(2.8, 2.1) | | | | |
| | 17,108 | 17,110 | $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ | 0.987 | 0.060 | 0.50 |
| | 19,062 | 19,070 | $\rightarrow {}^4G_{7/2}$ | | | |
| [SmB$_2$Cl$_3$]·2H$_2$O | 39,682, 48,070 | 40,486, 46,512<br>(2.7, 1.9) | | | | |
| | 23,790, 23,800 | | $^6I_{5/2} \rightarrow {}^4P_{9/2}$ | 0.990 | 0.054 | 0.60 |
| | 21,371 | 21,371 | $\rightarrow {}^4I_{9/2}$ | | | |
| | 20,836 | 20,838 | $\rightarrow {}^4I_{11/2}$ | | | |
| [DyB$_2$Cl$_3$]·3H$_2$O | 39,523, 47,620 | 41,152, 47,393<br>(2.8, 2.1) | | | | |
| | 7709 | 7712 | $^6I_{15/2} \rightarrow {}^6F_{11/2}$ | 0.992 | 0.059 | 0.71 |
| [HoB$_2$Cl$_3$]·2H$_2$O | 39,516, 46,834 | 40,842, 47,661<br>(2.6, 2.0) | | | | |
| | 22,106 | 22,111 | $^6I_8 \rightarrow {}^5G_6$ | 0.995 | 0.062 | 0.72 |
| | 27,694 | 27,700 | $\rightarrow {}^3G_6$ | | | |

[a] The covalence factors were calculated by the relations, $\bar{\beta} = \nu(\text{complexes})/\nu(\text{aquo})$, $b^{1/2} = [1/2(1-\beta)]^{1/2}$ and $\delta\% = 100(1-\bar{\beta})/\beta$ using the solid state spectra of complexes only.

Table 4. The binding energies (eV) of the ligand and its complexes

| | O 1*s* | | | C 1*s* | | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | $H_2O$ | C—OH | C═O | CH | C═O | Cl 2*p* | | Ln |
| Benzoin (B) | | 530.9 | 532.7 | 283.2 | 281.5 | | | |
| $[LaB_2Cl_3]\cdot 2H_2O$ | 534.1 | 532.0 | 533.4 | 283.6 | 280.1 | 197.2<br>197.3<br>197.5 | $3d_{5/2}$ | 835.2 |
| $[PrB_2Cl_3]\cdot 2H_2O$ | 534.2 | 532.1 | 533.3 | 283.8 | 280.2 | 197.4<br>197.5<br>197.7 | | 933.4 |
| $[NdB_2Cl_3]\cdot 4H_2O$ | 534.1 | 532.1 | 533.4 | 283.6 | 280.3 | 197.3<br>197.4<br>197.5 | | 984.3 |
| $[SmB_2Cl_3]\cdot 2H_2O$ | 534.4 | 532.0 | 533.2 | 283.5 | 280.2 | 197.3<br>197.5<br>197.4 | | 1084.1 |
| $[DyB_2Cl_3]\cdot 3H_2O$ | 534.5 | 532.4 | 533.1 | 283.7 | 280.1 | 197.4<br>197.5<br>197.8 | | 1298.0 |
| $[HoB_2Cl_3]\cdot 2H_2O$ | 534.4 | 532.5 | 533.4 | 283.8 | 280.2 | 197.3<br>197.4<br>197.5 | 4*d* | 162.5 |

### *X-ray photoelectron spectra*

The binding energy values for the ligand and the complexes are given in Table 4. It was noted that the Ln/Cl, Ln/O and Ln/C molar atomic ratios found from the chemical analysis and from the XPS data show very good agreement.

The lanthanide 3*d*- or 4*d*-electron binding energy is closely related to the central atom charge and therefore to its valency.[12] The oxygen 1*s* peaks of the complexes are asymmetric and their deconvolution yields three binding energy components coupling with hydroxylic, ketonic and water oxygen, relative to that in the ligand, indicating that the two hydroxyl group and two ketonic oxygens are in a symmetric form (Fig. 1). The signal due to carbon 1*s* is used as reference (284.6 eV) but, in addition, small peaks can be recorded at *ca* 283.8 and 280.1 eV for the complexes and 283.2 and 281.5 eV for the ligand, that should be ascribed to carbon atoms of the —CH— and C—O groups, respectively. The fact that the water molecules are uncoordinated can be checked again from the unchanged binding energy, as shown in Table 4. The chlorine 2*p* peak of the complexes is asymmetric and with an intensity ratio of 1 : 1 : 1, indicating that the three chlorine atoms are coordinated to lanthanide ion in unidentified form and the complexes are asymmetric.

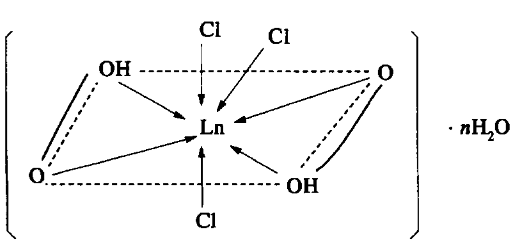

Fig. 1. The binding model of the complexes.

### *Fluorescence spectra*

The solid fluorescence spectra of the complexes of $Sm^{III}$, $Eu^{III}$, $Tb^{III}$ and $Dy^{III}$ are shown in Table 5, along with the assignments. It is found that the fluorescence properties are in line with each lanthanide ion, and $Tb^{III}$ complexes show the most intense green fluorescence.

### *Thermal behaviour*

TG and DSC techniques have been used to follow the thermal behaviour of the ligand and the complexes. According to the results obtained, the complexes are not volatile and their decomposition take place in similar steps. The main features of the complex $SmB_2Cl_3\cdot 2H_2O$ are summarized in Table 6.

The complexes obtained decompose exothermically in four main steps: the one corresponding to a loss of uncoordinated water at low

Table 5. The fluorescence data of solid Sm$^{III}$, Eu$^{III}$, Tb$^{III}$ and Dy$^{III}$ complexes

| Compound | $E_x$ (nm) | $E_m$ (nm) | Relative intensity | Assignment |
|---|---|---|---|---|
| Benzoin (B) | 510 | 433 | 2.47 | |
| $[SmB_2Cl_3]\cdot 2H_2O$ | 406 | 598 | 0.12 | $^5D_0 \rightarrow {}^7F_2$ |
| | | 645 | 0.13 | $\rightarrow {}^7F_1$ |
| | | 704 | 0.15 | $\rightarrow {}^7F_4$ |
| $[EuB_2Cl_3]\cdot H_2O$ | 320 | 593 | 6.72 | $^5D_0 \rightarrow {}^7F_2$ |
| | | 613 | 34.17 | $\rightarrow {}^7F_1$ |
| | | 699 | 8.11 | $\rightarrow {}^7F_4$ |
| $[TbB_2Cl_3]\cdot 2H_2O$ | 320 | 490 | 31.71 | $^5D_4 \rightarrow {}^7F_6$ |
| | | 545 | 109.71 | $\rightarrow {}^7F_5$ |
| | | 587 | 17.19 | $\rightarrow {}^3F_4$ |
| | | 621 | 16.10 | $\rightarrow {}^7F_3$ |
| $[DyB_2Cl_3]\cdot 3H_2O$ | 322 | 481 | 0.71 | $^4D_{7/2} \rightarrow {}^6F_{5/2}$ |
| | | 574 | 1.87 | $\rightarrow {}^6F_{13/2}$ |

Table 6. Thermal data for the ligand and complex $[SmB_2Cl_3]\cdot 2H_2O$

| | TG (DTG) | | Weight loss (%) | | DSC |
|---|---|---|---|---|---|
| Compound | $T$ (°C) | Process | Exp. | Theor. | $T$ (°C) |
| Benzoin (B) | 150–270 | decarbonization | 98.5 | 100 | 235 (exo.) |
| $[SmB_2Cl_3]\cdot 2H_2O$ | 60–115 | dehydration | 4.4 | 4.4 | 109 (exo.) |
| | 163–210 | | | | 206 (exo.) |
| | 210–265 | decarbonization | 54.2 | | 220 (exo.) |
| | 265–310 | | | | 295 (exo.) |
| | 310–475 | dehydrochlorination | 9.6 | | 306 (exo.) |
| | 475–615 | pyrolysis | 10.4 | | 600 (exo.) |
| | | | Σ78.6 | 78.9 | |

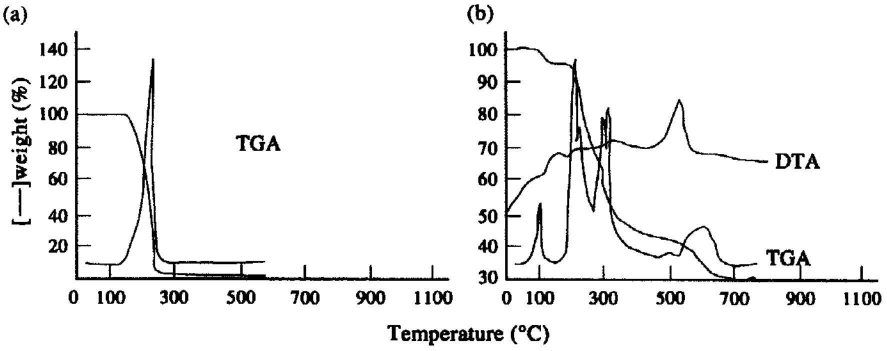

Fig. 2. Thermal diagrams of ligand (a) and $SmB_2Cl_3\cdot 2H_2O$ (b).

temperature, the second one probably corresponding to a decarbonization process, the third contact with the dehydrochlorination and the fourth the pyrolysis of the organic matter existing in these complexes (Fig. 2). The final product of the decomposition is lanthanide(III) oxide, as confirmed by X-ray diffraction and IR spectroscopy, as well as from the experimental and expected weight losses.

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