

Preparation and characterization of lanthanide (III) chloride complexes with benzothiazole

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ABSTRACT

A new series of complexes of lanthanide (III) complexes with Benzothiazole (BTZ) have been prepared in non-aqueous media and characterized by various physico-chemical studies, viz-elemental analysis, molecular weight, electrolyte conductance and I.R. Spectra etc. The their thermal properties have also been studied.

Key words: lanthanide (III) chloride complexes and benzothiazole.

A mixture of metal salts and ligand (BTZ) was dissolved in ethanol (molar ratio 1:5) and 2,2-dimethoxy propane was added as dehydrating agent and the reaction mixture was refluxed for half and hour on a water bath. On cooling a solid mass was obtained, which was washed, filtered and dried over anhydrous P_2O_5 .

The analytical data of newly prepared complexes clearly indicate the general composition of the complexes, $LnCl_3 \cdot 5BTZ$ (where $Ln=La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho$ or Yb). The monomeric nature and low values of molecular conductance data measured at room temperature in nitrobenzene, clearly indicates that all the three chloride ions are within the coordination sphere (Table 1). The similar behaviour is also supported by molecular weight data (Table 1). Due to closed shell electronic configuration lanthanum is found to be diamagnetic while all other tripositive lanthanide ions are paramagnetic. On complexation, the magnetic moment values of lanthanide ions remain almost unchanged (Table 1) indicating thereby that

4f-electrons do not participate in bond formation¹.

In IR spectra of the complexes, the negative shift of tertiary cyclic nitrogen of thiazole ring (BTZ) suggests that the cyclic nitrogen of ligand is involved in coordination (Table 2), where as the band appearing for cyclic sulphur do not show any shift, indicating the non-involvement of sulphur atom in co-ordination^{2,3} (Table 2). We have assigned a new band in far IR region to $\nu(Ln-N)$. The spectrum of the ligand is relatively transparent in this region⁴⁻⁵. A tentative coordination number eight has been assigned in all these complexes.

Thermo analytical data clearly indicates the absence of water molecules either in or out side the coordination sphere, and all the complexes are stable upto 170°C, 1.25 moles of ligands are lost in 210-300°C and 1 mole is lost in 370-425°C temperature range. Finally at Ca 520°C all the ligand molecules are lost. The residue obtained after heating to 730°C, to a constant weight is very close to that expected for the oxides.

Table 1: Analytical, molar conductance, molecular weight and magnetic moment data of lanthanide (III) chloride complexes of Benzothiazole

| S. No | complex | Analysis % found (Calc.) | | | | Ω (ohm ⁻¹ cm ² mole ⁻¹) | mole wt. found (Calc) | μ_{eff} B.M. |
|-------|--------------------------|--------------------------|------------------|----------------|----------------|--|-----------------------|------------------|
| | | M | C | G | N | | | |
| 1. | LaCl ₃ .5 BTZ | 18.18 (15.10) | 45.71 (45.62) | 2.80 (2.72) | 7.71 (7.60) | 4.3 | 907 (920.5) | Diamag |
| 2. | CeCl ₃ .5 BTZ | 15.26 (15.19) | 45.67 (45.57) | 2.81 (2.71) | 7.68 (7.59) | 3.5 | 908 (921.5) | 2.61 |
| 3. | PrCl ₃ .5 BTZ | 15.37 (15.28) | 45.62 (45.53) | 2.80 (2.71) | 7.69 (7.59) | 4.9 | 910 (922.5) | 3.64 |
| 4. | NdCl ₃ .5 BTZ | 15.67 (15.55) | 45.79 (45.38) | 2.79 (2.70) | 7.65 (7.56) | 2.8 | 914 (925.5) | 3.60 |
| 5. | SmCl ₃ .5 BTZ | 16.21 (16.10) | 45.19 (45.09) | 2.78 (2.68) | 7.60 (7.51) | 3.7 | 920 (931.5) | 1.77 |
| 6. | GdCl ₃ .5 BTZ | 16.81 (16.73) | 44.86 (44.75) | 2.77 (2.66) | 7.56 (7.46) | 2.9 | 925 (938.5) | 7.60 |
| 7. | TbCl ₃ .5 BTZ | 16.99 (16.91) | 44.75 (44.66) | 2.76 (2.66) | 7.55 (7.44) | 4.2 | 926 (940.5) | 9.42 |
| 8. | DyCl ₃ .5 BTZ | 17.32 (17.21) | 44.58 (44.49) | 2.75 (2.64) | 7.51 (7.42) | 3.1 | 930 (944) | 10.46 |
| 9. | HoCl ₃ .5 BTZ | 17.51 (17.43) | 44.48 (44.37) | 2.74 (2.64) | 7.48 (7.39) | 4.4 | 930 (946.5) | 10.40 |
| 10. | YbCl ₃ .5 BTZ | 18.21 (18.12) | 44.11 (44.00) | 2.73 (2.62) | 7.43 (7.33) | 4.9 | 945 (954.5) | 4.55 |

Table 2: Partical IR frequencies (Cm⁻¹) of lanthanide (III) chloride complexes of Benzothiazole

| S.No | Complex | ν C-S(Cyclic) | ν N(Cyclic) | ν Ln-N |
|------|--------------------------|-------------------|-----------------|------------|
| 1. | BTZ | 755m | 1370 V.S. | - |
| 2. | LaCl ₃ .5 BTZ | 750m | 1320s | 350m |
| 3. | CeCl ₃ .5 BTZ | 752m | 1325s | 355m |
| 4. | PrCl ₃ .5 BTZ | 755m | 1325s | 358m |
| 5. | NdCl ₃ .5 BTZ | 750m | 1315s | 352m |
| 6. | SmCl ₃ .5 BTZ | 758m | 1328s | 360m |
| 7. | GdCl ₃ .5 BTZ | 752m | 1315s | 35m |
| 8. | TbCl ₃ .5 BTZ | 750m | 1318s | 350m |
| 9. | DyCl ₃ .5 BTZ | 755m | 1322s | 358m |
| 10. | HoCl ₃ .5 BTZ | 758m | 1325s | 365m |
| 11. | YbCl ₃ .5 BTZ | 760m | 1330s | 365m |

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