

Lanthanide (III) bromide complexes of 2,2'-biquinoline mono N-oxide

S.K. GUPTA, V.K. DWIVEDI, P. SHARMA, D. THAKUR, A.K. SHARMA and S. THAKUR

Department of Chemistry, P.G.V. College, Jiwaji Ganj, (Lashkar), Gwalior - 474 001 (India).

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ABSTRACT

A new series of complexes of lanthanide (III) bromides with 2,2'-biquinoline mono N-oxide (Biquino) has been prepared in non-aqueous media and characterized through various physico-chemical studies.

Key words: Lanthanide (III), bromide complexes of 2,2'-biquinoline mono N-oxide.

Complexes were prepared by treating an ethanolic solution of lanthanide (III) bromide with ethanolic solution of Biquino (molar ratio 1:3). The reaction mixture was refluxed for half an hour. On cooling a solid mass was obtained which was washed filtered and dried over anhydrous calcium chloride.

The analytical data clearly indicates the general composition of the complexes $\text{LnBr}_3 \cdot 3$ Biquino (where Ln=La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho or Yb). The monomeric nature and low values of molecular conductance data clearly indicates that all the three bromide ions are non-ionic due to the closed shell electronic configuration of lanthanide ions. Lanthanum is found to be diamagnetic while all other tripositive lanthanide ions are paramagnetic. On complexation, the magnetic moment value of lanthanide ions remain almost unchanged indicating thereby that 4f-electrons do not participate in bond formation¹. In I.R. spectra of complexes, the negative shifting of N-O stretching vibrations (1240-1250 cm^{-1}) on complexation, which appears at ca 1270 cm^{-1} in free ligand, clearly indicates the co-ordination of oxygen to metal ions^{1,2}. The N-O

bending vibrations do not show any appreciable shifting and remain almost unchanged on complexation, appear at 850 cm^{-1} in free ligand. Co-ordination through nitrogen of the quinoline fragment of the ligand is suggested by the shifting of several frequencies attributed to C=C, C=N and ring vibrations occur in 1620-1400 cm^{-1} region, in free ligand. A positive shift has been observed in the vibration associated with C-H out of plane deformation due to tightening of the aromatic ring on complexation. We have assigned two new bands in 450-360 cm^{-1} region to $\nu(\text{Ln-N})$ and $\nu(\text{Ln-O})$ and assume it to be indicative of N-Oxide and amino nitrogen bonding to metal ions and the spectrum of ligand is relatively transparent in this region¹⁻⁶. Overall, I.R. spectra reveals that Biquino behaves as bidentate ligand forming a six membered chelate ring. A tentative co-ordination number 9 has been assigned in all these complexes.

Thermoanalytical data clearly indicates the absence of water molecules either in or out side the co-ordination sphere, and all the complexes are stable upto 190°C, 1.5 moles of ligands are lost in 210-300°C and 1.0 mole is lost in 360-425°C

temperature range. Finally at Ca 520°C all the ligand molecules are lost. The residue obtained after heating to 750°C, to a constant is very close to that expected for the oxides.

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