

Circular Dichroism of Lanthanide(III) Complexes

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There have been reported a number of studies on the circular dichroism (CD) of metal complexes with optically active ligands. However, these studies have been limited to the absorption bands due to the d-d transitions; no studies of the Cotton effect associated with the absorption due to the f-f transitions have ever been reported, except for magnetic optical rotation studies.¹⁾ Katzin and Barnett²⁾ have suggested the appearance of the Cotton effect of the tartarato complexes of some lanthanide(III) ions in an alkaline aqueous solution, but they have not yet shown any experimental data. In this paper we will report the results of the CD measurements of some lanthanide (III) complexes with optically active ligands.

The measurements have been carried out on aqueous alkaline solutions of tartarato-, lactato-, alaninato-, serinato- and valinato complexes of neodymium(III) and propylen ediamine tetraacetato complexes of praseodymium(III), neodymium(III) samarium(III), dysprosium(III) and erbium(III). The circular dichroism was clearly observed in the region of each absorption band (one of which is shown in Fig. 1), even though the intensity is very weak compared with that of a d-complex. This is to be expected from the fact that the f-electrons in lanthanide(III) complexes are better shielded than d-electrons in ordinary

transition metal complexes. In some cases the results were rather ambiguous because of too weak intensities.

As may be seen in Fig. 1, a few CD components

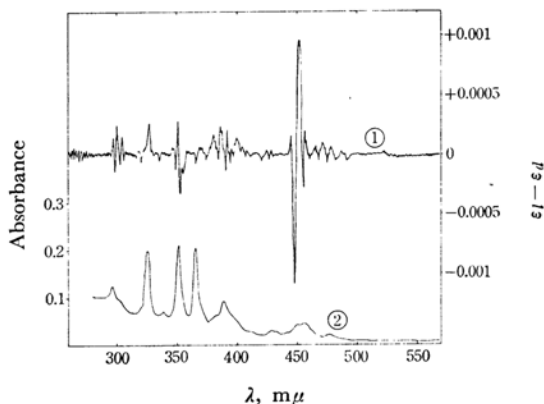


Fig. 1. CD and absorption spectra of levo-propylenediamine tetra acetato complex of dysprosium(III) in aqueous solution (0.1 F, pH=10.63), 1 cm. cell. 25°C.

(1) CD spectrum (2) Absorption spectrum

are observed for each absorption band; these components may be attributable to the ligand-field splitting. It is interesting that the absorption bands due to f-f transitions can be resolved into so minute peaks by CD measurements.

A more detailed discussion will be reported later.

1) For instance, Y. R. Shen, *Phys. Rev.*, **133** (2A), 511 (1964).

2) L. I. Katzin and M. L. Barnett, *J. Phys. Chem.*, **68**, 3779 (1964).