SYNTHESIS AND SPECTROSCOPY
OF HIGH AND LOW SYMMETRY
LANTHANIDE COMPLEXES

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SYNTHESIS AND SPECTROSCOPY OF HIGH AND LOW SYMMETRY LANTHANIDE COMPLEXES

高對稱與低對稱鐳系複合物的合成與光譜

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Abstract

The neat and diluted high symmetry hexachloroelpasolites Cs₂NaLnCl₆ (Ln=Nd, Ho) have been prepared. The high-resolution spectra of these two series of chloroelpasolites together with the fluoroelpasolites (Cs₂NaYF₆; Ln; Ln=Yb, Er) were recorded down to 10 K and analyzed carefully. The derived energy levels from the spectra have been calculated using crystal field theory.

Four series of low symmetry lanthanide complexes were synthesized and the crystal structures of some compounds were determined. The spectroscopic studies of these complexes were done to study the effects of coordination ligands on the vibrations and the energy levels of the central f-electrons. The following describes these complexes briefly.

1. New europium (III) and terbium (III) monodentate complexes with carbonyl group coordination have been prepared and characterized by X-ray and spectroscopic methods. Although the complexes comprise up to six coordinated water molecules they exhibit strong luminescence both in aqueous media and in the solid state. The high resolution, low temperature emission spectra are shown to be consistent with the crystallographic data.

2. The crystallographic and spectroscopic measurements for Ln[Au(CN)₂]₃·3H₂O (Ln=Pr, Sm, Eu, Tb) have been carried out. The emission spectra of Tb[Au(CN)₂]₃·3H₂O are unusual for a lanthanide ion because no new bands appear between 10 K to room temperature, although relative intensities do change. The analysis of extensive, well-resolved vibronic structures in the emission spectra has clearly shown the inadequacy of a theoretical intensity model which only considers IR active vibrational modes since both IR and Raman active vibrations were observed.
3. Seven trivalent praseodymium complexes derived from \textit{para}-substituted benzoic acids have been synthesized. The crystal structures of 5 complexes were determined by X-ray crystallography. The vibrational spectra of the complexes have been recorded and interpreted. The energy levels of central lanthanide ions could be deduced from the electronic spectra, and the electro-inductive effect of the functional groups of the ligands on the f-electrons has been investigated under the guide of the Hammett substituent constants.
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