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# A Terbium Chlorobismuthate(III) Double Salt: Synthesis, Structure, and Photophysical Properties

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## Abstract

We report on the structure and luminescence of a double salt trivalent rare earth ion acceptor, Tb<sup>3+</sup>, with octahedral [BiCl<sub>6</sub>]<sup>3-</sup> donor clusters. The novel TbBiCl<sub>6</sub>•14H<sub>2</sub>O (**1**) was prepared from aqueous BiOCl and TbCl<sub>3</sub>•6H<sub>2</sub>O. The crystal structure of compound **1** exhibits isolated [BiCl<sub>6</sub>]<sup>3-</sup> and [Tb(OH<sub>2</sub>)<sub>8</sub>]<sup>3+</sup> clusters. Luminescence data show energy transfer from octahedral chlorobismuthate(III) clusters to rare earth metal ions. Density Functional Theory (DFT) calculations show distinctly different emission pathways at high and low excitation energies.

## 1. Introduction

Rare earth metal ions produce sharp emission bands making them particularly useful in a variety of applications, including optoelectronics, biosensors, and photovoltaic compounds.<sup>1-7</sup> The challenge in developing viable materials using these ions centers on the difficulty of excitation of the lanthanide *f* electrons. The *f* orbitals are held close to the nucleus below the *d* orbitals due to lanthanide contraction and *f-f* transitions are symmetrically forbidden.<sup>8</sup> This results in weak emission intensities from these ions. Much research has focused on improving the emission intensity of solid state crystals<sup>9-11</sup> Energy transfer to rare earth metal centers is a

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