

Many transition metal complexes have characteristic colors. This means that there is absorption in the visible part of the spectrum resulting from an electron being excited by visible light from a level occupied by an electron in a molecular orbital of the complex to an empty level. If the energy difference between the orbitals capable of transition is set to ΔE , the absorption frequency ν is given by $\Delta E = h\nu$. Electronic transitions by optical pumping are broadly classified into two groups. When both of the molecular orbitals between which a transition is possible have mainly metal d character, the transition is called a **d-d transition** or **ligand-field transition**, and absorption wavelength depends strongly on the ligand-field splitting. When one of the two orbitals has mainly metal character and the other has a large degree of ligand character, the transition is called a **charge-transfer transition**. Charge transfer transitions are classified into metal (M) to ligand (L) charge-transfers (MLCT) and ligand to metal charge-transfers (LMCT).

example, a d^3 complex $[\text{Cr}(\text{NH}_3)_6]^{3+}$ shows two d-d absorptions in the 400 nm (25000 cm^{-1}) region, suggesting that the complex has two groups of molecular orbitals between which an electronic transition is possible with a high degree of transition probability. This means that, when three electrons in the t_{2g} orbital are excited to the e_g orbital, there are two energy differences due to repellent interactions between the electrons.

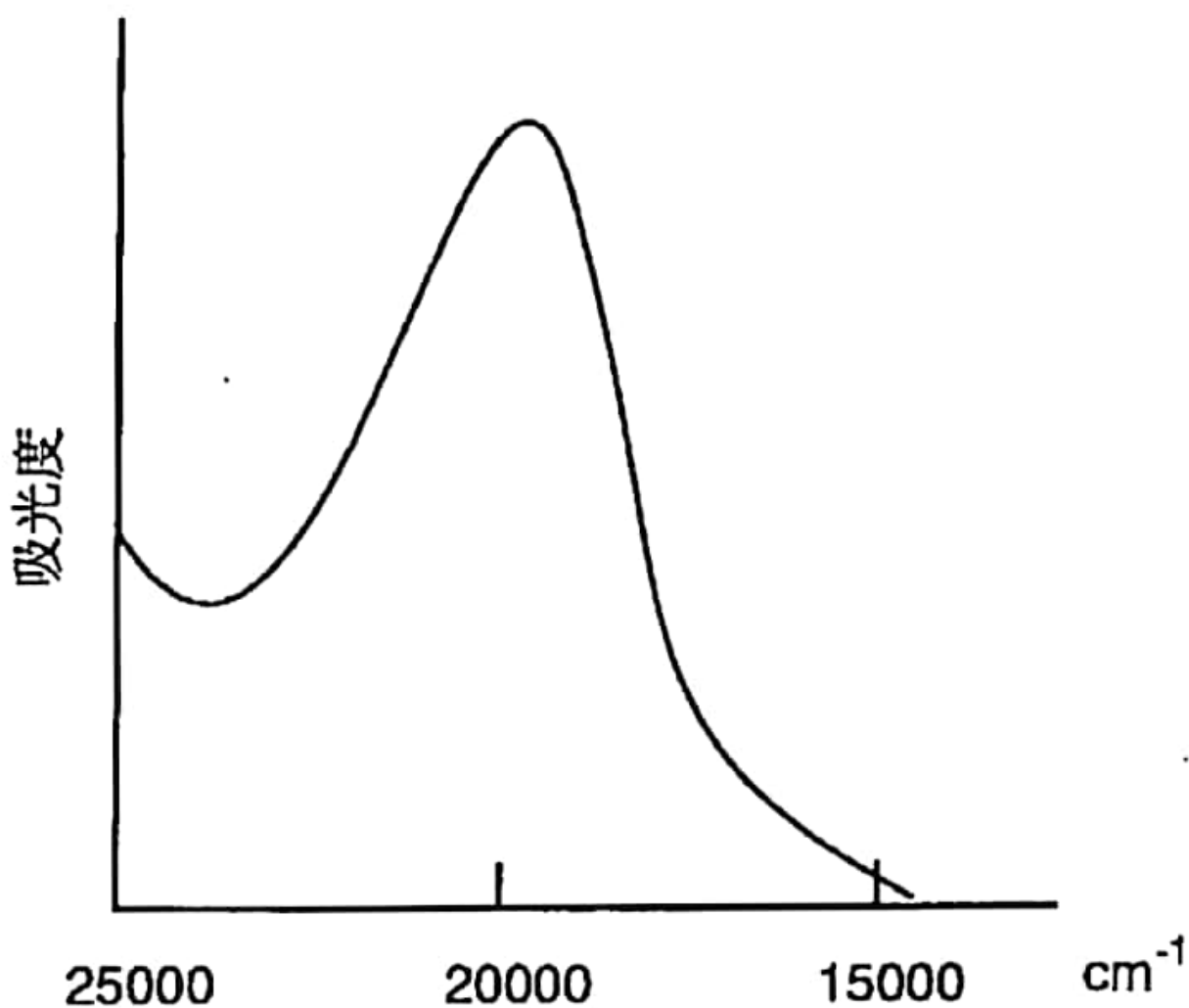


Figure 6.3.13: - A visible absorption spectrum of $[\text{Ti}(\text{OH}_2)_6]^{3+}$.

Since the analysis of the spectra of octahedral complexes is comparatively easy, they have been studied in detail for many years. When a complex has only one d electron, the analysis is simple. For example, Ti in $[\text{Ti}(\text{OH}_2)_6]^{3+}$ is a d^1 ion, and an electron occupies the t_{2g} orbital produced by the octahedral ligand field splitting. The complex is purple as the result of having an absorption at 492 nm (20300 cm^{-1}) (Figure 6.13) corresponding to the optical pumping of a d electron to the e_g orbital. However, in a complex with more than one d electrons, there are repellent interactions between the electrons, and the d-d transition spectrum has more than one absorptions. For example, a d^3 complex $[\text{Cr}(\text{NH}_3)_6]^{3+}$ shows two d-d absorptions in the 400 nm (25000 cm^{-1}) region, suggesting that the complex has two groups of molecular orbitals between which an electronic transition is possible with a high degree of transition probability. This means that, when three electrons in the t_{2g} orbital are excited to the e_g orbital, there are two energy differences due to repellent interactions between the electrons.