ON THE QUENCHING OF TRIVALENT TERBIUM LUMINESCENCE LIGANTE LOW LYING TRIPLET STATE ENERGY. THE [Tb(tta)₃ 2H₂O] CASE

*<u>A. S. Souza</u>^a, L. A. Nunes^b, M. C. F. C. Felinto^c, H. F. Brito^d, O. L. Malta^a ^aDepartamento de Química Fundamental, Universidade Federal de Pernambuco, 50670-901, Recife PE, Brazil Instituto de Física, Universidade de São Paulo, 13560-970 São Carlos SP, Brazil ⁶ Instituto de Pesquisas Energéticas e Nucleares, 05505-800 São Paulo SP, Brazil ^d Instituto de Química, Universidade de São Paulo, 05508-900 São Paulo SP, Brazil * Corresponding author: oscar@inct-inami.com.br

Highlight

The luminescence quenching in Tb complexes with low lying triplet state energies is rationalized in terms of intramolecular energy transfer involving mainly the 7F_5 state, instead of the 7F_6 ground state of the Tb $^{3+}$ ion.

The description of the processes which follow the absorption of light by organic ligand and energy transfer (ET) to the lanthanide ion that emits in the visible is one of the most important problems in the design of luminescent lanthanide complexes. In Tb^{3+} complexes whit the energy of the ${}^5\mathsf{D}_4$ state very close to the ligands triplet energy levels (T_1) , luminescence quenching is observed due to efficient back transfer (BT). A typical case is the [Tb(tta)₃ 2(H₂O)] complex. It is known that in this complex at room temperature both Tb luminescence and ligand phosphorescence are practically absent, and only at low temperature they are weakly observed [1]. The ET from T_1 to the 5D_4 level, in principle, requires the Tb^{3+} ion to be initially in the $^{7}F_{6}$ ground state, once the $^{7}F_{1}$ excited levels are not thermally populated. However, curiously enough, the 7 F₅ level has an unusual long lifetime [2] and, in the present case, the 5 D₄ \rightarrow 7 F₅ transition is in excellent resonance conditions with the ligand phosphorescence peak. Taking into account the selection rules on the total angular momentum quantum number (J) [3], these facts strongly suggest that ET and BT occur efficiently through the exchange mechanism involving the 7 F₅ level. Fig. 1 shows the energy level scheme used in setting up an appropriate system of rate equations to describe the level populations.

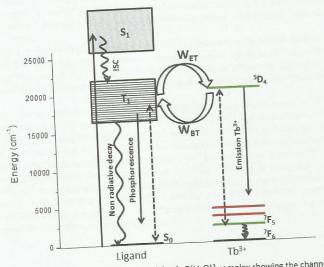


Figure 1. Energy level diagram for the $[Tb(tta)_3 2(H_2O)]$ complex showing the channel for the energy transfer (W_{ET}) and back transfer (W_{BT}) process

The calculated transfer rate for the exchange mechanisms is $2.7 \times 10^7 \text{ s}^{-1}$. Numerical estimates of the 5D_4 decay-curve are in good agreement as compared to the experimental results.

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References:

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