

Synthesis and Luminescence Spectra of Eu³⁺-Tris(thenoylacetylacetonate) Complexes Co-coordinated by N- and O-Donor Ligands

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Introduction

In the last few years the interest in lanthanoid chelates as light emitting materials for photonic applications¹⁻⁴, such as light emitting diodes (LED) and optical fibres, has increased remarkable. Rare earth complexes consist of the central lanthanoid ion surrounded by organic ligands which act as chromophores. By the introduction of organic chelate ligands high quantum efficiencies can be achieved. Moreover, broad excitation bands caused by the conjugated aromatic systems occur and narrow defined emission lines from the rare earth ions can be observed. The effect of the organic ligand is known as "antenna effect"⁵ (Fig. 1)

To obtain complexes with high quantum efficiencies it is necessary to choose organic molecules with pronounced internal conversion (IC), efficient energy transfer from the ligand to the metal ion, and an efficient luminescent ion. For these reasons, we chose trivalent Europium as a red line emitter and as chromophores β -diketonates in combination with 2,2'-Bipyridyl, 1,10-Phenanthroline, and Pyridyl derivatives. (Fig. 2)

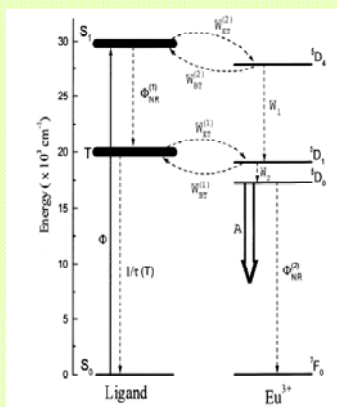


Fig. 1: Mechanism of the luminescence and energy transfer in Eu³⁺ complexes⁶

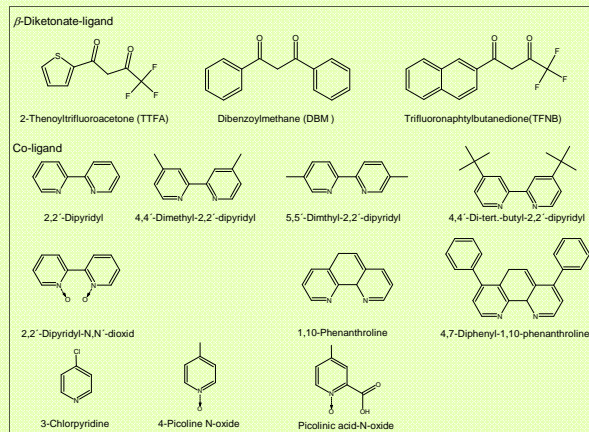


Fig. 2: Overview of applied ligands

LM = H₂O, EtOH, DMF, CH₃CN

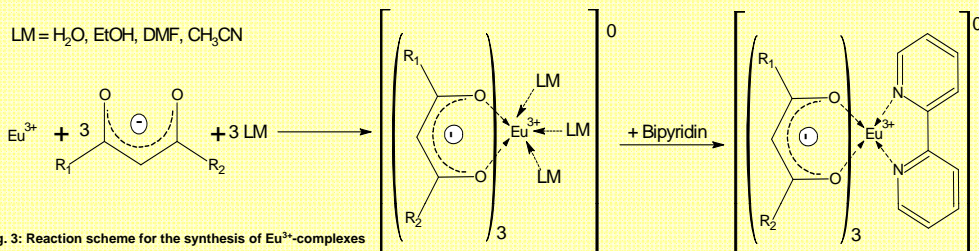


Fig. 3: Reaction scheme for the synthesis of Eu³⁺-complexes

Synthesis

The reactions were carried out in ethanol or a mixture of ethanol and acetonitrile in two steps. First the β -diketonate complexes were synthesised, which are still coordinated by two or three solvent molecules. The second step is a ligand exchange, wherein the solvent ligands were replaced by the neutral organic ligand. (Fig. 3)

Results and Conclusions

Two reaction products (1 and 2) yielded suitable crystals for X-ray single crystal analysis which gave the supposed crystal structures. (Fig. 4 and 5)

Both complexes comprise an square-antiprismatic coordinated metal ion, whereby the Eu-N bond length of (2) is about 0.04 Å longer than in (1) (Tab. 1), which can be described by electron density and by steric effects. All complexes were also characterised by infrared spectroscopy and elemental analysis (Carbon and Sulphur) which were in line with the calculated values according to the crystal structure.

The broad excitation bands (220 nm to 480 nm) can be assigned to the ligand metal charge transfer (Fig. 6). The most intense emission line of Eu³⁺ is located at 613 nm. The effect of the neutral co-ligand X on the quantum efficiency of [Eu³⁺(TTFA)₃X] is tremendous (Tab. 2) and can be explained by the relative position of the triplet state to the excited states of Eu³⁺.

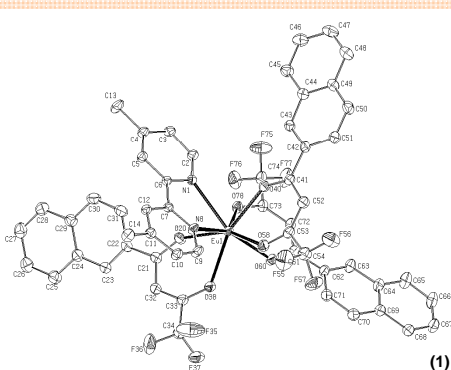


Fig. 4: Crystal structure of [Eu(TFNB)₃(4,4'-di-methyl-2,2'-dipyridyl)]

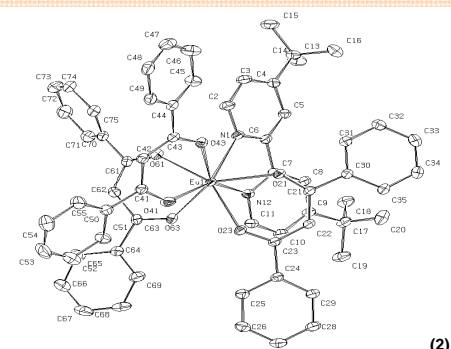


Fig. 5: Crystal structure of [Eu(DBM)₃(4,4'-di-tert-butyl-2,2'-dipyridyl)]

	[Eu ³⁺ (TFNB) ₃ (4,4'-Me ₂ -Bipy)] [†] (013)	[Eu ³⁺ (DBM) ₃ (4,4'-di-tert-Butyl-Bipy)] [†] (018)
Crystal system	monoclinic	triclinic
Space group	P2 ₁ /n	P-1
a [Å]	11.4415 (2)	9.9614 (3)
b [Å]	27.8037 (5)	12.3377 (4)
c [Å]	15.1932 (3)	22.9123 (8)
α [°]	90	80.123 (5)
β [°]	104.690 (5)	87.474 (5)
γ [°]	90	68.624 (5)
Ø r (Eu-O) [Å]	2.37	2.37
Ø r (Eu-N) [Å]	2.56	2.60
N-Eu-N angle [°]	62.60	61.41

Tab. 1: Crystallographic data for (1) and (2)

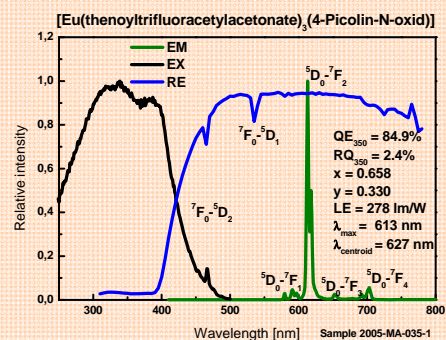


Fig. 6: Excitation, emission and reflection spectra of [Eu³⁺(TTFA)₃(4-Picolin-N-oxide)]

Co-ligand	QE ₃₅₀ [%]
3-Chloropyridine	10.9
H ₂ O	20.8
Picolinic acid-N-oxide	44.7
4,7-Diphenyl-1,10-phenanthroline	46.7
2,2'-Dipyridyl-N,N'-dioxide	61.4
4,4'-Dimethyl-2,2'-dipyridyl	73.5
4-Picoline-N-oxide	84.9

Tab. 2: Quantum efficiencies of [Eu³⁺(TTFA)₃X] complexes with different neutral ligands X

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