Structural and photophysical properties of europium(III) mixed complexes with β-diketonates and o-phenanthroline

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Abstract

The luminescence of solid samples of europium mixed complexes with β-diketonates and o-phenanthroline (Phen), EuL$_3$Phen, is investigated at 77 K in order to probe the structure of these compounds. A ligand-to-metal energy transfer process is evidenced. The quantum yields of 10^{-5} M solutions in CH$_2$Cl$_2$ are measured relative to 9,10-dichloroanthracene. Except for benzylacetonate, these yields are quite low, due to the presence of low-lying electronic states of the ligands. The crystal structure of Eu(NO$_3$)(DBM)$_2$(TBPO)$_2$ as well as its photophysical properties in CH$_2$Cl$_2$ solution are presented.

1. Introduction

Lanthanide chelates with β-diketonates have always attracted a large interest since they may be used for many applications such as solvent extraction agents, NMR shift reagents, laser materials [1] or luminescent labels in fluoroimmunoassays [2]. In particular, the now sought-after antenna effect [3] was demonstrated for the first time on Eu and Tb diketonates [4]. In this effect, the organic ligand acts as an efficient photon absorber through its ππ* transition. The electromagnetic energy is then transferred to the lanthanide ion from an excited singlet or triplet state which is best in resonance with the $^5D_0$(Eu) or $^5D_4$(Tb) states. The latter are long-lived states and emit in the visible part of the spectrum, which has definite advantages when the lanthanide ions are used as spectroscopic probes. The luminescence spectra of many Eu and Tb tris(β-diketonates) have been studied with respect to the substituent effects on intramolecular energy transfer [5] and crystal field splitting [6]. In these chelates, the Ln^{III} ions have a coordination number of 6 and are not always well protected from solvent interaction. This is the main reason why we started an investigation of mixed complexes in which the coordination number is

increased to 8 by addition of an o-phenanthroline (Phen) or triphenylphosphine oxide (TPPO) ligand [7–10]. In this communication, we investigate the photophysical properties and the relative quantum yields of EuL$_3$Phen complexes in which L is an aryl-substituted β-diketonate (see Scheme 1). A comparison is made with a compound in which Phen is substituted by tributylphosphine oxide (TBPO).
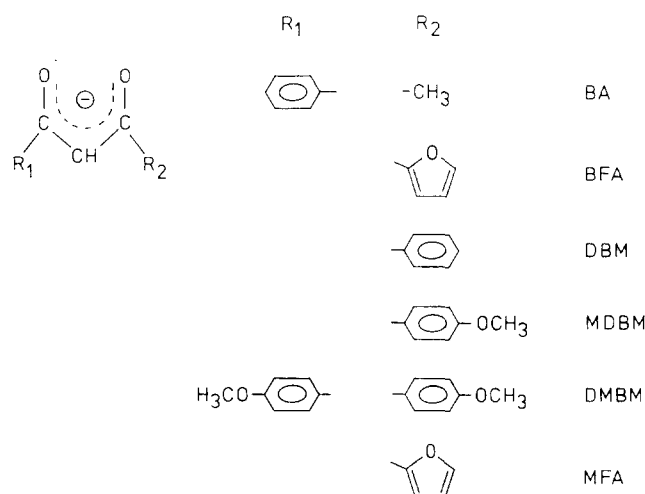
Scheme 1.

2. Experimental details

2.1. Synthesis and analysis of the complexes

EuL₃Phen complexes: 3 mmol of β-diketone and 1 mmol of Phen in 10 ml EtOH were dissolved and mixed; 1 mmol of $LnCl_3 \cdot nH_2O$ (Ln = Eu and Eu + Gd for Eu-doped Gd compounds) in 10 ml of EtOH was added under stirring; the pH was adjusted to 6 with ethanolamine; the pale yellow precipitates were filtered, washed with ethanol, recrystallized in acetone and dried in vacuo. Elemental analyses are reported in Table 1. The complexes were further characterized by their vibrational spectra.

2.2. Spectroscopic measurements

Infrared spectra were measured as KBr pellets on an Alpha Centauri FT IR spectrometer from Mattson. Electronic absorption and emission spectra were usually gathered on both Eu and Eu-doped (2%) Gd complexes. Absorption spectra were recorded with a Perkin Elmer Lambda 5 spectrometer while reflectance spectra were measured as 5% dispersions in MgO on a Perkin Elmer Hitachi PE-340 spectrometer (reference, MgO pellet). Luminescence measurements were performed using a previously described set-up [11]. Relative emission intensities were corrected for the instrumental response of the spectrometer [12]. Finely powdered microcrystalline samples were measured at 295 and 77 K and solutions 10^{-2} to 10^{-6} M in freshly distilled and degassed CH_2Cl_2 (Fluka, puriss) at 295 K. Relative quantum yields were determined for 10^{-5} M solutions upon excitation at 385 nm (this wavelength was chosen on the basis of the excitation spectra). Both the absorption and emission spectra were measured immediately after preparing the degassed solutions. The band area of the $^5D_0 \rightarrow {}^7F_J$ transitions with $J = 0-4$ only were taken into consideration. Since we report relative quantum yields and since the intensity of $^5D_0 \rightarrow {}^7F_5$ and $^5D_0 \rightarrow {}^7F_6$ transition are quite weak, the relative error introduced is small (<5%). A solution of 9,10-dichloroanthracene (Fluka, puriss) was measured under the same experimental conditions and was taken as reference.

2.3. Structure determination

Measurements were performed at 230 K on a Syntex R3M four-cycle diffractometer. Crystal data: $C_{54}H_{76}EuNO_9P_2$, $M = 1097.12$, tetragonal uniaxial prisms, space group $P\bar{4}2_1c$, $a = b = 25.904(6)$ Å, $c = 16.510$ Å, $V = 11078(5)$ Å³, $Z = 8$, $D_c = 1.32$, graphite monochromatized Mo Kα radiation (0.71073 Å), μ(Mo Kα) = 12.4 cm^{-1}. Data collection and refinement, cf. [13]; 2710 unique reflections were available for refining 364 parameters. All phenyl and alkyl groups were considered isotropic and only the Eu coordinates were refined anisotropically. The final R_f value was 0.095. During the data collection, the intensities of five standard reflections were monitored; after an increase of 10%, they faded to about 80% of their initial values. Data were corrected accordingly.

3. Results and discussion

3.1. EuL₃Phen complexes

Reflectance minima for Eu microcrystalline samples and absorption maxima for both Eu and Eu-doped Gd solutions 10^{-5} M in CH_2Cl_2 are reported in Table 2 while typical spectra are displayed in Fig. 1. Besides weak f-f transitions at 536 and 468 nm ($^5D_1 \leftarrow {}^7F_0$, $^5D_2 \leftarrow {}^7F_0$), the reflectance spectra of the Eu complexes display one broad band in the spectral range 450–240 nm. Its maximum shifts from 330 nm (BA) to 375–380 nm (DBM, MDBM, DMBM) and 390 nm (MFA). The solution spectra exhibit two main bands. One at

TABLE 1. Elemental analyses of the mixed complexes

Compound	Found (%)				Calculated (%)			
	C	H	N	Ln	C	H	N	Ln
Eu(BA)₃Phen	61.46	4.26	3.35	18.60	61.84	4.33	3.44	18.63
Gc(BA)₃Phen[a]	61.14	4.43	3.24	19.40	61.45	4.30	3.41	19.15
Eu(DBM)₃Phen	68.44	4.17	2.72	15.93	68.33	4.13	2.80	15.17
Gd(DBM)₃Phen[a]	67.66	4.21	2.74	15.90	67.97	4.10	2.39	15.61
Eu(MDBM)₃Phen	65.77	4.33	2.44	14.15	65.99	4.34	2.68	13.92
Gd(MDBM)₃Phen[a]	65.20	4.29	2.53	14.56	65.68	4.32	2.66	14.33
Eu(DMBM)₃Phen	63.69	4.81	2.37	13.22	64.02	4.52	2.37	12.86
Gd(DMBM)₃Phen[a]	63.98	4.40	2.38	13.71	63.73	4.50	2.36	13.24
Eu(MFA)₃Phen	61.05	4.03	–	14.32	61.08	3.89	2.97	14.33
Eu(DBM)₂(NO₃)(TBPO)	59.28	7.26	1.11	–	59.11	6.98	1.28	13.85

[a]Gd compounds contain 2% Eu.

TABLE 2. Absorption maxima of EuL₃Phen complexes and of Eu(NO)₃(DBM)₂(TBPO)₂

L	Solids[a]			10^{-5} M solution in CH_2Cl_2			
	λ_{min} (nm)			λ_{max} (absorbance) (nm)			
BA	300sh	330	360sh	268	296sh	318	
DBM	305sh	380		264	292sh	352	373sh
MDBM	305sh	375	400sh	272	290sh	356	385sh
DMBM	305sh	380	410sh	274	292sh	360	380sh
MFA	300sh	390		276	292sh	366	386sh
[b]	305sh	385		274	282sh	364	400sh

[a]Microcrystalline powders, reflectance spectra. [b]Eu(NO)₃-(DBM)₂(TBPO)₂.
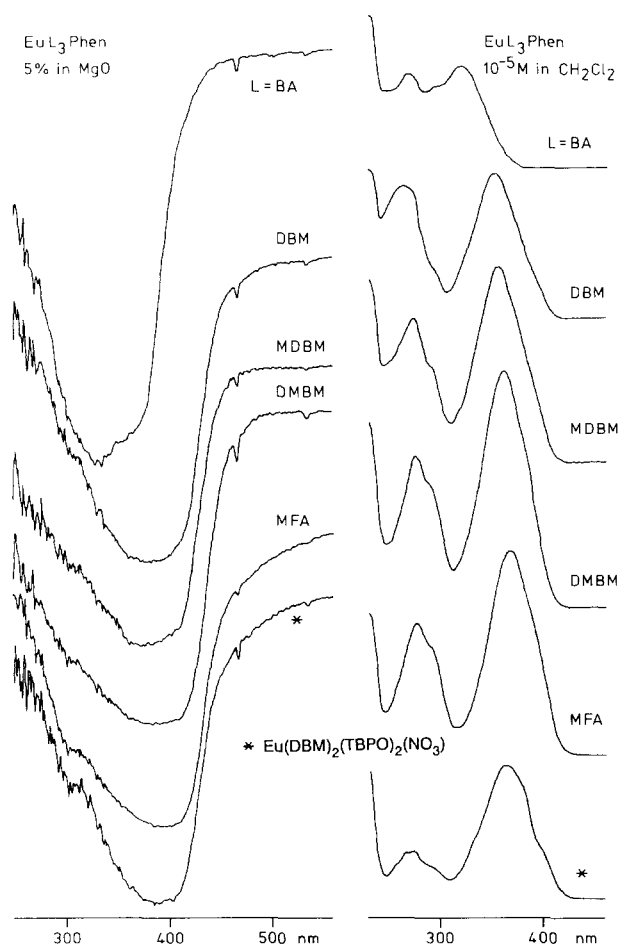
Fig. 1. Reflectance (left) and absorption (right) spectra of EuL₃Phen and Eu(NO₃)(DBM)₂(TBPO)₂.

264–276 nm is more or less substituent-independent while the other one is shifted from 318 nm (BA) to 366 nm (MFA). Both are assigned to $\pi\pi^*$ transitions of the conjugated systems of Phen and L, respectively. The significant red shift observed between solid state and solution spectra has recently been attributed to a saturation phenomenon occurring in the crystalline form [14]. It is noteworthy that the addition of the Phen

ligand does not perturb the β-diketonate electronic system much, since the corresponding transitions in LnL₃ complexes are found at 343 nm (DBM), 358 nm (MDBM) and 364 nm (DMBM). Similarly to what was reported earlier [6], the β-diketone $\pi\rightarrow\pi^*$ absorption band undergoes a marked bathochromic shift when the size of the conjugated system is increased in going from a methyl to a phenyl, a methoxyphenyl or a furyl substituent. The progressive para-substitution of the aromatic rings by methoxy groups slightly increases the bathochromic effect.

In previous papers, we have discussed the detailed luminescence spectra of EuL₃Phen [7] and R₄NEuL₄ [8] complexes as well as the crystal field splittings induced by the coordination of DBM and DMBM [8,10]. Here, we compare the luminescence intensities and lifetimes of the investigated complexes in order to show their structural similarity. Indeed, all the emission spectra obtained upon ligand excitation (Fig. 2, Table 3) display similar shapes pointing to metallic sites lying in analogous chemical environments. The differences observed in both the ⁷F_J splittings and the bandwidths are small and arise from slight variations in the crystal field potential. No difference was found between the Eu and Eu-doped Gd complexes, pointing to molecular compounds in which the complex moieties are well isolated from each other. The $^5D_0 \leftarrow {}^7F_0$ excitation spectra reveal substantial differences; at 77 K, relatively sharp bands are observed for BA (580.22 nm, full width at half height (FWHH) = 0.09 nm) and for DBM (580.4 and 580.18 nm, FWHH = 0.1 nm), while broader bands with shoulders are observed for MDBM (580.14 and 580.28(sh) nm, FWHH = ca. 0.6–0.7 nm) and for MFA (580.12 and 580.28(sh) nm, FWHH = ca. 0.2 nm). The relative corrected intensities of the $^5D_0 \rightarrow {}^7F_J$ transitions at 77 K are similar for all the complexes investigated, except Eu(MDBM)₃Phen for which the hypersensitive

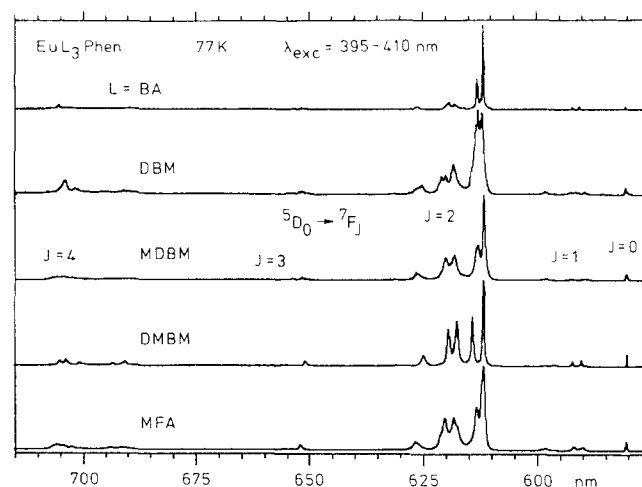
Fig. 2. Luminescence spectra of microcrystalline samples of EuL₃Phen obtained under ligand excitation (385–420 nm).

TABLE 3. Corrected relative intensities of the $^5D_0 \rightarrow {}^7F_J$ transitions, lifetimes of the Eu($^5D_0$) level, and quantum yield of EuL$_3$Phen complexes, upon excitation through the ligand band (intensities, quantum yield 385–420 nm) or through the $^5D_0 \leftarrow {}^7F_0$ transition (lifetimes, 574–580 nm)

L	I_{rel} ($^5D_0 \rightarrow {}^7F_J$)[a]					τ_{obs} (77 K) (ms)	τ_{obs} (295 K)[a] (ms)	ϕ_F (295 K)[b] (%)
	$J = 0$	1	2	3	4			
BA	0.2	1.0	17.8	0.6	1.6	0.63(2)	0.61(2)	
	0.3	1.0	19.3	0.6	2.1	–	0.55(3)	6.4
DBM	0.2	1.0	18.1	0.5	2.4	0.52(3)	0.43(2)	
	0.3	1.0	25.0	0.7	2.2	–	0.12(2)	1.6
MDBM	0.4	1.0	27.6	0.7	2.3	0.45(1)	0.37(2)	
	0.4	1.0	24.7	0.6	1.9	–	0.13(1)	0.2
DMBM	0.2	1.0	16.9	0.6	1.7	0.42(2)	0.34(2)	
	0.4	1.0	27.8	0.9	2.5	–	0.14(2)	0.6
MFA	0.3	1.0	17.7	0.7	1.8	0.53(2)	0.47(2)	
	0.3	1.0	24.8	0.6	1.8	–	0.14(1)	0.1

[a]First line microcrystalline samples; second line 10^{-3} M solutions in CH$_2$Cl$_2$. [b]Quantum yields of 10^{-5} M solutions in CH$_2$Cl$_2$, relative to 9,10-dichloroanthracene.

transition $^5D_0 \rightarrow {}^7F_2$ is substantially more intense. At 295 K, the latter is the largest due to an increase in vibronic effects, which are especially marked when a methoxy substituent is added. Schmidt and Butter [15] have shown that Eu(DBM)$_3$Phen crystallizes in the same monoclinic $P2_1/c$ space group as Eu(acac)$_3$Phen, the coordination polyhedron being a distorted square antiprism. A similar Eu environment probably prevails in the EuL$_3$Phen samples investigated in this work and one may conclude that the coordination polyhedron around the metallic ion is not significantly affected by the substituents of the β-diketonate.

The solution spectra are usually alike the solid state spectra, pointing to a solution structure similar to the solid state structure. However, there is a marked tendency for the hypersensitive transition to be more intense, which we attribute to an increased mixing of the electronic 4f states with vibrational states. This effect is reflected in the $^5D_0 \leftarrow {}^7F_0$ excitation spectra: all the bands are centered around 580 nm and their FWHH ranges between 1.1 and 1.3 nm. Moreover, a significant red shift of the maxima is observed upon varying the concentration from 10^{-5} to 10^{-2} M; it may arise from a self-extinction phenomenon or from some aggregation of the metal ion complexes.

The Eu($^5D_0$) lifetimes (Table 3) confirm the above analysis. In the solid state at 77 K, the replacement of the methyl moiety by either a phenyl or a furyl substituent lowers τ_{obs} from 0.6 to 0.5 ms. Introducing methoxy substituents in *para* position reduces these lifetimes further by *ca*. 10%. Finally, except for ligand BA, the lifetimes of the $^5D_0$ state are significantly shorter in solution than in the solid state at the same temperature. This might be explained either by a larger conformational lability in solution or by a shortening of the

triplet state lifetime of the ligand, which, in turn, favours non-radiative pathways.

The quantum yields ϕ_F of 10^{-5} M solutions, relative to 9,10-dichloroanthracene (quantum yield in benzene 0.71 [16]) are reported in Table 3. They reflect the decrease in lifetime observed for the solutions and correspond roughly to the ability of the substituent to favour low-lying electronic states; *cf*. the 360–420 nm range in the absorption spectra reported in Fig. 1. An absorption from a charge transfer state, which is known to quench the Eu luminescence efficiently [17], might also be present in this spectral range.

3.2. Eu(NO$_3$)(DBM)$_2$(TBPO)$_2$

The transparent, fibrous looking crystals did not diffract well. Moreover, it appeared that a transition between a tetragonal and an orthorhombic phase occurs around 170 K and partially destroys the crystals. Above this temperature, the associated process is already active so that it was not possible to solve the structure entirely. The compound is comprised of isolated molecular entities, with the two DBM molecules coordinated laterally and the TBPO molecules bonded above and underneath. The Eu coordination polyhedron is irregular and completed by a bidentate nitrate ion (Fig. 3). The Eu–O distances (Table 4) span a large range (2.31–2.52Å), with an average value of 2.44(8) Å. The calculated ionic radius for Eu^{III}, 1.13(8) Å is somewhat larger than the expected value for an 8-coordinate ion, 1.07 Å.

In contrast to the thenoyltrifluoroacetone–trioctyl-phosphine oxide–Eu^{III} system in hexane, for which a detection limit of 6–7 ng/l has been achieved for Eu [18], solutions of Eu(NO$_3$)(DBM)$_2$(TBPO)$_2$ in CH$_2$Cl$_2$ are weakly luminescent. The quantum yield of a 10^{-5} M solution is less than 0.01% relative to 9,10-dichloro-
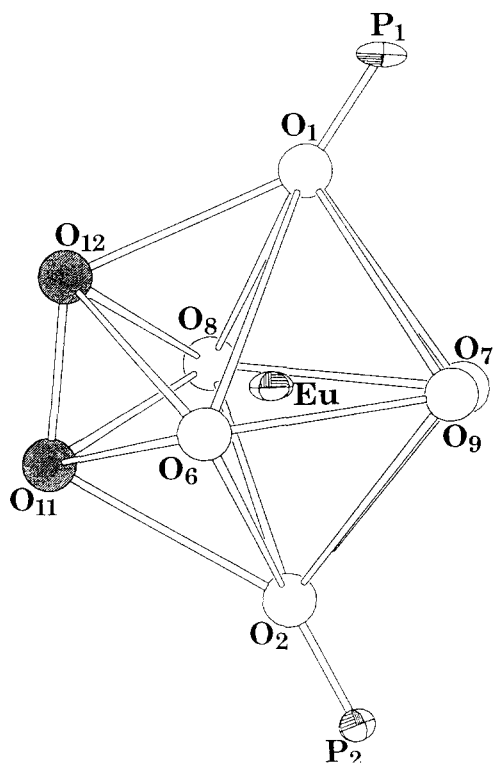
Fig. 3. Coordination polyhedron in $Eu(NO_3)(DBM)_2(TBPO)_2$ as obtained from X-ray crystal structure determination. Atom numbering scheme: O_1 and O_2 from TBPO, O_{11} and O_{12} from NO_3^-, O_6, O_8 and O_7, O_9 from DBM molecules.

TABLE 4. Selected bond lengths (Å) in $Eu(NO)_3(DBM)_2(TBPO)_2$, with standard deviation on the last digit between parentheses

Eu–O_1	2.33(2)	Eu–O_7	2.47(2)
Eu–O_2	2.31(2)	Eu–O_8	2.51(2)
Eu–O_{11}	2.50(2)	Eu–O_9	2.52(2)
Eu–O_{12}	2.48(3)	P_1–O_1	1.48(2)
Eu–O_6	2.39(2)	P_1–O_2	1.51(2)

anthracene, again consistent with the trend observed for EuL_3Phen complexes.

4. Conclusion

At low temperature, solid samples of the compounds investigated display an intense and characteristic luminescence. In solution, however, and with the exception of $Eu(BA)_3Phen$, efficient quenching processes take

place, which may be related to the presence of low-lying electronic states of the ligand extending down to $24\,000\;cm^{-1}$.

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