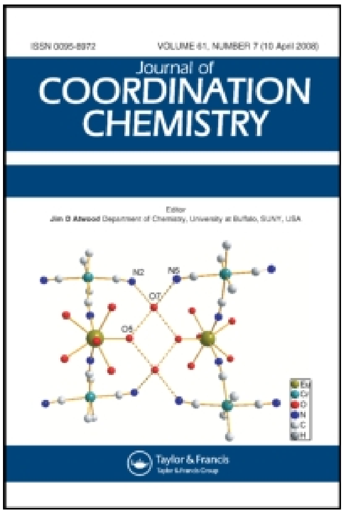

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EUROPIUM(III) AND TERBIUM(III) β-DIKETONATE ADDUCTS WITH 2,6-DIMETHYLMORPHOLINE: SYNTHESIS, CHARACTERIZATION AND EMISSION SPECTRA

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EUROPIUM(III) AND TERBIUM(III) β-DIKETONATE ADDUCTS WITH 2,6-DIMETHYLMORPHOLINE: SYNTHESIS, CHARACTERIZATION AND EMISSION SPECTRA

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Complexes with composition $Ln_2(\beta\text{-diketonate})_6 \cdot (dmm)$ (Ln = Eu, Tb; dmm = 2,6-dimethylmorpholine; β-diketonate = 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanodionate (tta); 4,4,4-trifluoro-1-phenyl-1,3-butanodionate (tfpb) and 1,1,1-trifluoro-1,4-pentanedionate (tfa)) have been synthesized. The adducts were characterized by microanalyses, IR spectra and emission spectra at room temperature and at 77 K. The spectra of europium complexes indicate the oligomeric at least dimeric, nature of the compounds, since the bands are broad. The number of peaks in all cases was interpreted as C_{3v} symmetry around the central ion.

Keywords: Europium(III); terbium(III); emission spectra; β-diketonate; dimethylmorpholine

INTRODUCTION

Emission spectra of europium(III) β-diketonate complexes with N-bases have been described. The following compounds have been studied: $Eu(fod)_3 \cdot 2H_2O$ (Hfod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione); $Eu(fod)_3 \cdot 2(1\text{-Mepipz})$ (1-Mepipz = 1-methylpiperazine);

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$Eu(dppd)_3 \cdot 2(pyz)$ (Hdppd = 1,3-diphenyl-1,3-propanodione, pyz = pyrazole); $Eu(dppd) \cdot 0.5$(1-Mepipz); $Eu(dppd_3) \cdot$ (1-Phpipz) (1-Phpipz = 1-phenylpiperazine); $Eu(pd)_3 \cdot (2H_2O)$ (Hpd = 2,4-pentanedione); $Eu(pd)_3 \cdot$ 2(py) (py = pyridine); $Eu(pd)_3 \cdot 0.5$(1-Mepipz) and $Eu(pd)_3 \cdot$ (1-Phpipz).[1] Related studies were previously published.[2–4]

In this article a systematic study of the emission f–f spectra of the complexes with composition $Ln_2(\beta\text{-diketonate})_6 \cdot (dmm)$ (Ln = Eu, Tb; dmm = 2,6-dimethylmorpholine; β-diketonate = 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanodionate (tta); 4,4,4-trifluoro-1-phenyl-1,3-butanodionate (tfpb) and 1,1,1-trifluoro-1,4-pentanedionate (tfa)) are described. The objective was to characterize the adducts and determine the symmetries in the europium complexes, since the compounds could be obtained only in microcrystalline form (hence the lack of X-ray studies) and also to obtain spectra of the terbium compounds, since all are good emitters and thus potentially interesting phosphors.

EXPERIMENTAL

The diketonates were prepared by the general reaction given below:

$$\begin{aligned} &LnCl_3 \cdot xH_2O + 3(\beta\text{-diketone}) + 3NH_3 \\ &\quad \rightarrow Ln(\beta\text{-diketone})_3 \cdot yH_2O + x - y(H_2O) + 3NH_4Cl \end{aligned}$$

($x = 2,3$; β-diketone = 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanodione (Htta); 1,1,1-trifluoro-2,4-pentanedione (Htfa) and 4,4,4-trifluoro-1-phenyl-1,3-butanodione (Htfpb)).

The syntheses involved addition of an ethanolic solution of the hydrated europium(III) or terbium(III) chloride to the solution of diketone in ethanol (molar ratio slightly greater than 1 : 3). Separation of the chelates occurred at pH = 6–7, which was obtained by dropwise addition of a concentrated ammonia solution. The chelate thus formed was filtered and dried in air. In some cases an oily product separated, crystallizing after about one day.

The preparation of the adducts containing 2,6-dimethylmorpholine (dmm) was accomplished by reaction of the chelates with base in 1 : 4 ratio, using ethyl ether as solvent. The mixture was stirred for 54 h. The solution thus formed was evaporated almost to dryness and the product filtered. The compounds are air stable, non-hygroscopic and more soluble than the chelates. All compounds were characterized by CHN microanalytical procedures. The lanthanides were estimated by a gravimetric method in which a known weight of the compound was ignited to its oxide above 800°C. These analyses were cross-checked by EDTA titrimetry using xylenol orange as indicator.

Infrared absorption spectra were recorded using Nujol and KBr pellets on Hitachi 270-90 and Birad-'DV' 64 IR spectrophotometers. Proton NMR spectra were obtained in $CDCl_3$, CCl_4 and a mixture of $CDCl_3$ and d^6-DMSO on Bruker AC-300 and Hitachi 5-1500 FT NMR spectrometers, using TMS as an internal standard. Europium and terbium luminescence spectra were recorded on a Hitachi Perkin-Elmer MPF-4 spectrofluorimeter both at room temperature and 77 K.

RESULTS AND DISCUSSION

Analytical data in Table I indicate the following stoichiometry for the adducts: $Ln_2(\beta\text{-diketonate})_6 \cdot (dmm)$. Melting points and yields are also shown.

Infrared absorption spectra for all compounds were recorded and appear in Table II. νNH was not observed, since this frequency appears in the same region than CH_3 and CH_2 stretching bands.

TABLE I Analytical data of compounds

Compound	*MP* (°C)	*Yield* (%)	*Elemental Analyses* (%)							
			Ln		*C*		*H*		*N*	
			Theor.	*Exp.*	*Theor.*	*Exp.*	*Theor.*	*Exp.*	*Theor.*	*Exp.*
$Eu_2(tta)_6 \cdot (dmm)$	155	86	17.40	17.27	37.14	37.66	2.13	2.17	0.80	0.90
$Eu_2(tfpb)_6 \cdot (dmm)$	147–148	72	17.77	17.41	46.35	46.32	2.86	2.89	0.81	0.80
$Eu_2(tfa)_6 \cdot (dmm)$	156	70	22.72	22.86	32.32	32.07	2.78	2.60	1.04	1.24
$Tb_2(tta)_6 \cdot (dmm)$	155	78	18.05	18.17	36.85	36.70	2.11	2.03	0.79	0.76
$Tb_2(tfpb)_6 \cdot (dmm)$	153	80	18.43	18.38	45.98	46.12	2.86	2.46	0.81	0.81
$Tb_2(tfa)_6 \cdot (dmm)$	157	68	23.51	22.85	31.99	32.60	2.75	2.67	1.03	1.50

TABLE II IR spectral analyses data (cm^{-1})

Compound	$\nu C{=}O$		νCF	$\nu_{as}COC$	$\nu sCOC$
$Eu_2(tta)_6 \cdot (dmm)$	1660sb	1620m	1165b	1120b	820m
$Eu_2(tfpb)_6 \cdot (dmm)$	1660sb	1620w	1160b	1120b	800w
$Eu_2(tfa)_6 \cdot (dmm)$	1665s	1625s	1175b	1130b	830m
$Tb_2(tta)_6 \cdot (dmm)$	1665s	1625s	1160b	1130b	835m
$Tb_2(tfpb)_6 \cdot (dmm)$	1600sb	1620m	1170b	1130b	800w
$Tb_2(tfa)_6 \cdot (dmm)$	1660sb	1620m	1165b	1120b	825m

s = strong; b = broad; m = medium; w = weak.

NMR spectra for the complexes were recorded and the observed signals correspond to: one CH_3, quartet at 1.2–1.3 ppm (TMS); three signals due to six ring hydrogens at 2.6 (doublet, 2H), 3.1 (doublet, 2H) and 3.9 (singlet, 2H) ppm; one very broad NH signal between 9 and 10 ppm, confirming the existence of this group. In the chelates, C=CH protons appear at 6.54 ppm ($Eu(tfpb)_3$); 5.98 ppm ($Eu(tfa)_3$); 6.26 ppm ($Tb(tfa)_3$) and 6.77 ppm ($Tb(tfpb)_3$). In the adducts, all signals due to the chelate protons are very weak. In the case of the protons discussed above, they could not be observed, because there is a very large signal at *ca.* 7.2 ppm, due to $CHCl_3$, present in all spectra (probably due to isotope exchange with $CDCl_3$, a solvent used in all cases).

Figures 1 and 2 show the emission spectra of two europium complexes, $Eu_2(tta)_6(dmm)$ and $Eu_2(tfpb)_6(dmm)$. In both cases one $^5D_0 \rightarrow {}^7F_0$ peak was observed, three peaks due to the $^5D_0 \rightarrow {}^7F_1$ and three or more peaks due to the $^5D_0 \rightarrow {}^7F_2$ transitions (see Table III). They are broad and badly

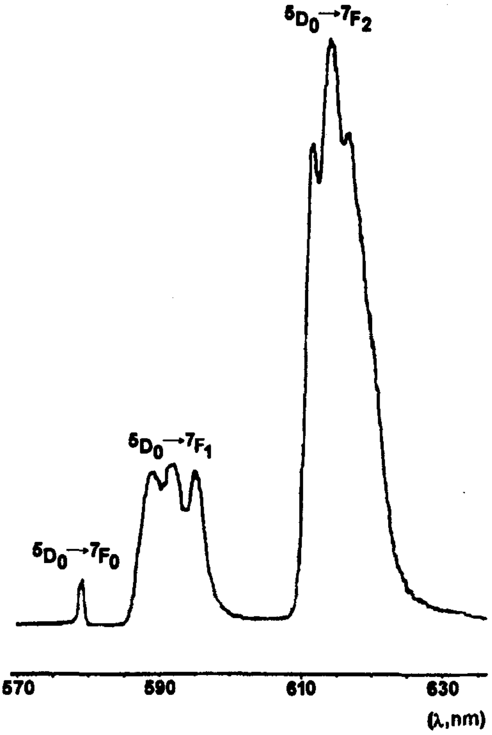

FIGURE 1 Emission spectrum of $Eu_2(tta)_6(dmm)$, solid state, 77 K.

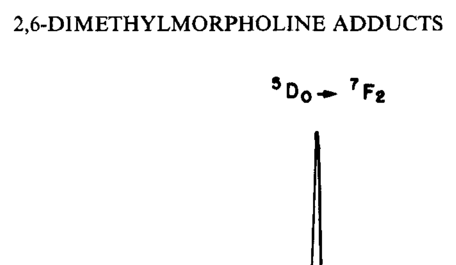

FIGURE 2 Emission spectrum of $Eu_2(tfpb)_6(dmm)$, solid state, 77 K.

TABLE III Emission spectral data (nm) for the compounds of europium and terbium

Compound	$^5D_0 \rightarrow {}^7F_0$	$^5D_0 \rightarrow {}^7F_1$	$^5D_0 \rightarrow {}^7F_2$	
$Eu_2(tta)_6 \cdot (dmm)$	579.2	589.0, 591.7, 595.0	611.5, 614.2, 616.8	
$Eu_2(tfpb)_6 \cdot (dmm)$	579.0	589.0, 591.7, 595.5	611.3, 613.5, 616.0	
$Eu_2(tfa)_6 \cdot (dmm)$	579.3	588.5, 592.0, 595.5	610.5(sh), 612.5, 614.5, 616.2, 617.7(sh)	
Compound	$^5D_4 \rightarrow {}^7F_6$	$^5D_4 \rightarrow {}^7F_5$	$^5D_4 \rightarrow {}^7F_4$	$^5D_4 \rightarrow {}^7F_3$
$Tb_2(tta)_6 \cdot (dmm)$	489.5	541.7, 544.0	583.7	622.0
$Tb_2(tfpb)_6 \cdot (dmm)$	487.5	541.3, 544.0	582.0	623.5
$Tb_2(tfa)_6 \cdot (dmm)$	487.7	542.5, 544.5	623.0	623.0

resolved, but the number and spectral region of the peaks can be interpreted as triple splitting of the $^7F_1$ level (one A and one E species) and an A and two E species for the $^7F_2$ level, with non-resolved E-species splittings. These results indicate C_{3v} symmetry around the europium(III) ions[5] and the

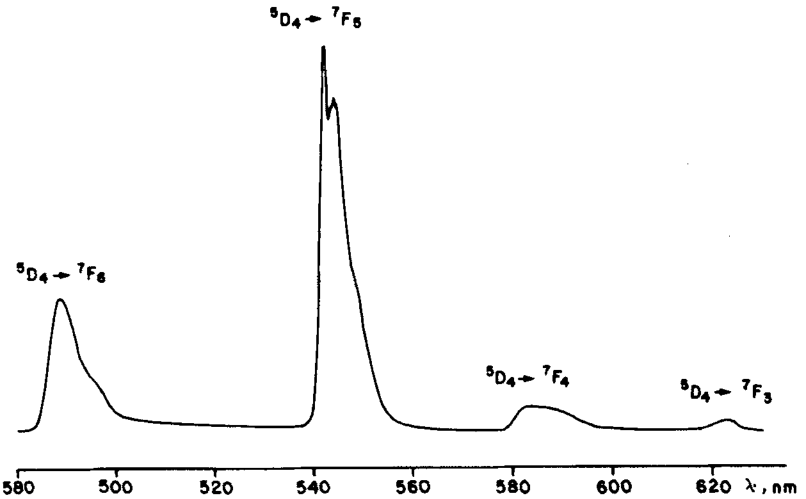

FIGURE 3 Emission spectrum of $Tb_2(tfa)_6(dmm)$, solid state, 77 K.

existence of polymeric or at least dimeric species. This attribution is also based on the similarity of the emission spectra with those of analogous compounds previously studied with known structures.[1]

Figure 3 presents the luminescence spectrum of $Tb_2(tfa)_6(dmm)$, where the transitions $^5D_4 \rightarrow {}^7F_{6,5,4,3}$ can be observed. All spectra of terbium compounds are very similar (Table III). All europium and terbium complexes are strongly luminescent, thus making these compounds potentially interesting phosphors.

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