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Luminescence and crystal-field fitting of two optical isomeric complexes of europium

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ABSTRACT

FT-IR and Raman vibrational spectra and electronic emission spectra have been recorded for enantiomers of europium complexes with DBM: dibenzoylmethanate **1**,**2**, and TTFA: 2-thenoyltrifluoroacetonate **3**,**4**, employing the chiral ligands $\mathbf{L}_{SS}$(+)- and $\mathbf{L}_{RR}$(-)-4,5-pinene bipyridine. Contrary to the previously published X-ray data, where geometrical differences were stated to occur for particular enantiomers, the vibrational (and the emission) spectra of the individual optical isomers of a complex are not distinguishable. Using excitation into the Eu^{3+} $^5D_2$ multiplet term, the emission intensity is weak from $^5D_1$, whereas a complex structure is observed for the $^5D_0 \rightarrow {}^7F_J$ transitions. Features in the vibronic sidebands exhibit similar derived vibrational energies to those observed in the Raman spectra. Fittings of 25 $4f^6$ crystal-field energy levels of **2** and **4** have been attempted with some approximations concerning the local Eu^{3+} environments. The $^5D_0$ emission lifetimes are monoexponential and are 0.5 (**1**,**2**) and 0.9 ms (**3**,**4**) at room temperature.

1. Introduction

Excited-state energy transfer between enantiomers comprising rare earth ions has received attention in several solution studies [1–4]. The optical isomers can be distinguished by magnetic circularly polarized luminescence and this has also been employed in solution studies of enantiomers [5]. Although low-temperature, high-resolution emission spectra of solid-state racemic mixtures of rare earth complexes have been reported and analyzed (e.g. Refs. [6,7]), the corresponding detailed spectra for individual isomers have seldom been investigated.

In the present study, two pairs of europium enantiomers have been subjected to detailed spectroscopic examination. The previously reported X-ray crystallographic data for one pair of isomers showed distinct differences from mirror-image symmetry [8]. The major purpose of this study was therefore to probe the spectral distinctions that we anticipated from these differences in reported bond distances and geometry for the enantiomers. There were two other aims of this study. The rich vibronic sidebands in the spectra have been investigated using the hypersensitive $^5D_0$–$^7F_2$ transition of Eu^{3+} and a comparison has been accomplished with infrared and Raman vibrational data in order to investigate the vibrational activities of the modes which contribute most vibronic intensity. Finally, since most crystal-field calculations for lanthanide ion systems have been carried out for rather simple complexes, data for the crystal fields acting in these more complex 8-coordinate systems were also of interest.

For the first pair, using the chiral ligands $\mathbf{L}_{SS}$(+)- and $\mathbf{L}_{RR}$(-)-4,5-pinene bipyridine, the complexes with formula $[Eu(DBM)_3\mathbf{L}]$ ($\mathbf{L}_{SS}$ in **1**, $\mathbf{L}_{RR}$ in **2**; DBM dibenzoylmethanate) have been investigated. The syntheses and crystal structures have been reported [8] and the structures are schematically shown in Fig. 1 (top). The second pair of enantiomers were constructed using the same chiral ligands ($\mathbf{L}_{SS}$ in **3**, $\mathbf{L}_{RR}$ in **4**), but with 2-thenoyltrifluoroacetonate (TTFA) instead of DBM: $[Eu(TTFA)_3\mathbf{L}]$ (Fig. 1 (bottom)). The syntheses and crystal structures of **3** and **4** have been reported [9]. The space group for each complex is $P2_1$ and there are 2 Eu^{3+} ions within the (Bravais) unit cell which are related by symmetry operations. The Eu^{3+} site symmetry is C_1 but its 8-fold coordination by oxygen and nitrogen represents a distorted square antiprism. The coordination environment of Eu^{3+} in each case includes two nitrogen atoms of the chiral bipyridine derivative.

2. Experimental

Following the syntheses of **1**–**4** [8,9], the analytical data for 4 replicate analyses (with standard deviations) are as follows: **1** $[Eu(DBM)_3\mathbf{L}_{SS}]$ Expt. N 2.62 ± 0.04; C 69.96 ± 0.69; H 4.65 ± 0.05.

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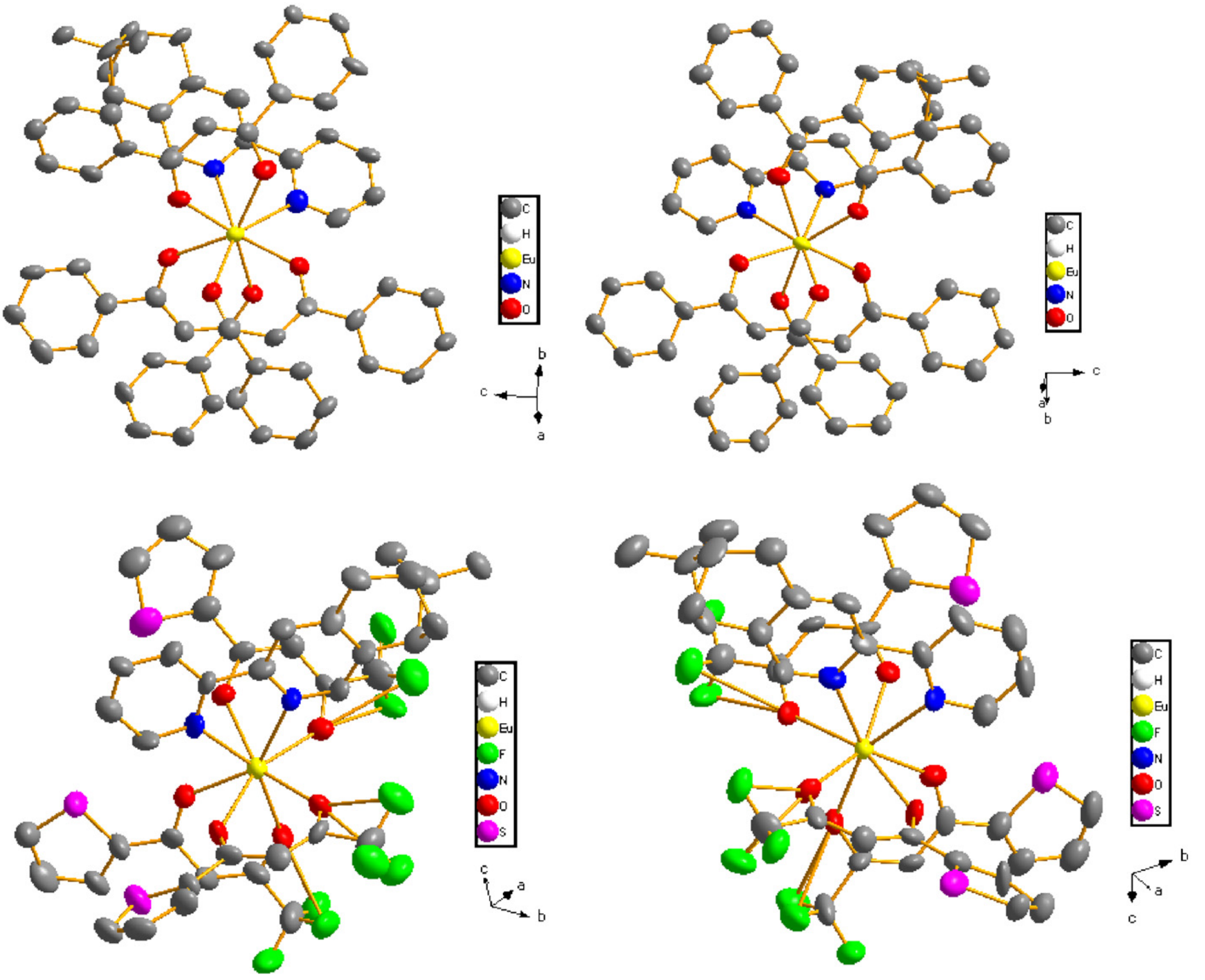

Fig. 1. Structures of [Eu(DBM)$_3$L] (L$_{SS}$(+) in **1** (top right), L$_{RR}$(−) in **2** (top left)) and [Eu(TTFA)$_3$L] (L$_{SS}$(+) in **3** (bottom right), L$_{RR}$(−) in **4** (bottom left)). Note that all hydrogen atoms are omitted for clarity.

Calc. N 2.61; C 69.45; H 4.79; **2** [Eu(DBM)$_3$**L**$_{RR}$] Expt. N 2.62±0.03; C 70.06±0.69; H 4.58±0.15. Calc. N 2.61; C 69.45; H 4.79; **3** [Eu(TTFA)$_3$**L**$_{SS}$] Expt. N 2.63±0.03; C 46.33±0.46; H 2.75±0.03. Calc. N 2.63; C 46.57; H 2.84; **4** [Eu(TTFA)$_3$**L**$_{RR}$] Expt. N 2.66±0.05; 46.60±0.46; H 2.76±0.03. Calc. N 2.63; C 46.57; H 2.84.

FT-IR spectra were recorded at room temperature using nujol mulls and KBr discs by a Nicolet FT-IR instrument with resolution 4 cm^{-1}. Similar results were obtained; hence only the latter spectra are reported herein. Room-temperature Raman spectra were recorded by a Perkin Elmer Spectrum 2000 spectrometer using a resolution of 4 cm^{-1}. Emission spectra were recorded with the samples housed in an Oxford instruments closed-cycle cryostat using various laser excitation lines selected by a Panther optical parametric oscillator system pumped by the second harmonic of a Surelite Nd:YAG laser. The emission was detected by a SpectruMM CCD camera situated on an Acton 0.5 m monochromator. Single crystals were not sufficiently large to permit the use of circularly polarized radiation on oriented samples. Room-temperature excitation spectra were measured by a Horiba Jobin Yvon Fluorolog spectrofluorometer using a xenon lamp as the light source and a TBX-04-A single-photon detection module. For lifetime measurements, the emission was analyzed with a 0.25 m Jobin–Yvon monochromator and the signal was detected by a Hamamatsu R636 photomultiplier.

3. Results and discussion

The FT-IR and Raman spectra of **1**–**4** are shown in Fig. 2 and it is not possible to distinguish the enantiomers **1**,**2** or **3**,**4** from the vibrational spectra. The FT-IR spectra are particularly complex and the strongest bands were mentioned in Refs. [8,9]. Prominent features in the Raman spectra are (cm^{-1}) at 1598 ν(8a, phenyl)+ν(C=O), 1315 ν(C=C–C=O), 1280 ν(C–C=C), 1002 ν(12, phenyl) for [Eu(DBM)$_3$**L**], where the notation is from Ref. [10], and at 1601 ν(C=O), 1523, 1415, 1309 for [Eu(TTFA)$_3$**L**].

3.1. *Emission spectra of [Eu(DBM)$_3$L]: 1 and 2*

The unpolarized emission spectra recorded at 10 K using 454, 457, 460 and 465 nm excitation lines into $^5D_2$ levels were recorded in the range 14,000–19,000 cm^{-1} and were similar for both **1** and