ELSEVIER

Journal of Alloys and Compounds 275–277 (1998) 765–768

Journal of ALLOYS AND COMPOUNDS

Isomerism in the adduct of tris(4,4,4,-trifluoro-1-(2-naphthyl)-1,3-butanedionato)europium(iii) with dipyridyl

L.C. Thompson[a,*], F.W. Atchison[a], V.G. Young[b]

[a]Department of Chemistry, University of Minnesota, Duluth, MN 55812, USA
[b]Department of Chemistry, University of Minnesota, Twin Cities, Minneapolis, MN 55455, USA

Abstract

The title compound (conveniently abbreviated Eu(TAN)$_3$·dipy) has been crystallized from a chloroform/2-propanol solvent mixture to give two different forms. These have been characterized by luminescence spectroscopy and by X-ray diffraction. The two forms have different coordination polyhedra which means that they are structural isomers. One of them is best described as bicapped trigonal prismatic and the other, which contains two slightly different molecules, as square antiprismatic. © 1998 Elsevier Science S.A.

Keywords: Eu(TAN)$_3$·dipy; Chloroform/2-propanol mixture; Luminescence spectroscopy; X-ray diffraction

1. Introduction

Because of their labile nature, it has proved to be difficult to prepare classical complexes of the rare earth(III) ions in isolable isomeric forms. On the other hand, there are many examples of such complexes in which the crystal structure unequivocally contains at least two slightly different coordination polyhedra and at least one case in which there are four such 'isomers' [1]. Both Nd(tfa)$_3$·2H$_2$O [2] (tfa=the anion of trifluoroacetylacetone) and Eu(DPM)$_3$·DMOP [3] (DPM=the anion of dipivaloylmethane, DMOP=2,9-dimethyl-1,10-phenanthroline) are examples of complexes in which there are two very different structures in the crystal caused by the different arrangements of the chelate rings. In the former, both coordination polyhedra are dodecahedra, and in the latter they are both square antiprisms. In a study of the corresponding europium complex with tfa, Raven [4] was able to prepare crystals of two different types that had different luminescence spectra. Examination of these by X-ray diffraction showed that they were structural isomers and an analysis by the method of Porai-Koshits and Aslanov [5] gave the result that one of them is based on the dodecahedron and the other on the bicapped trigonal prism [6]. As far as we are aware, this is the only such example in a classical complex of the trivalent rare earth ions. We have prepared and characterized some 25 additional examples of adducts of the tris(β-diketonates) of europium(III) and by varying the substituents on the β-diketone have been able to prepare a number of molecules that have two or more 'isomers' in a single crystal. In this communication we report the second example of discrete, isolable isomers using a β-diketone having a trifluoromethyl group and a 2-naphthyl group as the substituents.

2. Experimental

The compound Eu(TAN)$_3$·dipy was prepared by dissolving the β-diketone and dipyridyl in a 3:1 mole ratio in the minimum amount of 95% ethanol. Slow addition of the stoichiometric amount of NaOH resulted in the neutralization of the acidic proton of the β-diketone. A concentrated ethanolic solution of Eu(NO$_3$)$_3$·6H$_2$O (one mole equivalent) was added dropwise, with stirring, over a period of 30 min. Precipitation was immediate and after 2 h of stirring, the light yellow product was isolated by filtration and dried. The compound is soluble in a number of solvents including acetonitrile, benzene, dichloromethane, chloroform, toluene, and ethylacetate and is insoluble in ethanol, hexane, cyclohexane, and 2-propanol. A sample recrystallized from a benzene/hexane mixed solvent was submitted for microanalysis: Calc. (Exp.): C, 56.58 (56.71); H, 2.92 (2.96); N, 2.54 (2.47). Luminescence spectra were obtained with a McPherson RS-10 spectrophotometer at 77 K using 365 nm excitation from a Hg lamp, as described previously [3]. The X-ray data were collected on an Enraf-Nonius CAD4 (blocks) or a Siemens

---

*Corresponding author.

0925-8388/98/$19.00
PII: S0925-8388(98)00436-8

SMART system (plates) and the cell constants were determined from a set of 25 reflections determined from a random search routine. The data were corrected for Lorentz and polarization effects and an absorption correction was determined and applied. The solution of the structure was obtained with the SHELXTL-Plus V5.0 suite of programs.

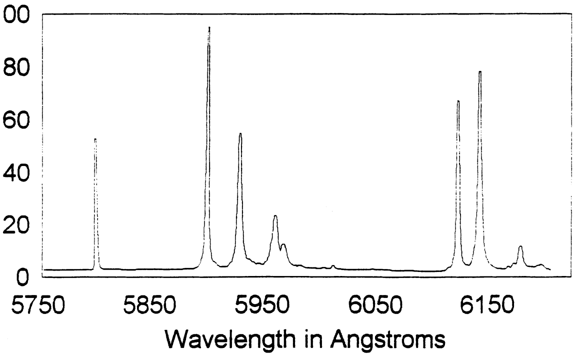

Fig. 1. Luminescence spectrum of the blocks.

3. Results

The chemical analysis shows that the desired compound was successfully synthesized. The existence of two transitions in the $^5D_0 \rightarrow {}^7F_0$ region of the luminescence spectrum (as well as multiple peaks in other regions) in one sample of the powdered crude product indicated the presence of more than one site for the europium(III) ion. Experience has shown that these crude preparations are often not analytically pure, and that conclusions regarding the formation of structural isomers must be drawn very carefully. The compound was recrystallized from a number of solvents and solvent mixtures. In some cases the luminescence spectrum indicated one type of site, in others a second type and, in still others, the presence of two types of crystals, one of each type. Recrystallization from chloroform/2-propanol yielded the two types of crystals (labeled ‘blocks’ and ‘plates’ for identification) which were then separated mechanically with tweezers and a magnifying glass. (Analytically pure samples of the blocks can also be obtained from benzene/hexane mixtures but we were not successful in obtaining analytically pure samples of the plates alone.)

The luminescence spectra of the two types of crystals are different and are presented in Figs. 1 and 2. Although it always appears that the plates contain a small contamination from the blocks, the differences are clearly evident in that the $^5D_0 \rightarrow {}^7F_0$ transitions occur at 580.3 nm for the blocks and 580.7 nm for the plates. The blocks had a melting point of 192–193°C, whereas the plates had a melting point of 166–172°C and appeared to contain solvent. (The presence of 0.5 mol of non-coordinated 2-propanol in the lattice was later confirmed by the X-ray study.)

A sample of the blocks obtained from benzene/hexane

Table 1
Crystal data and structure refinement

	Plates	Blocks
Empirical formula	$C_{52}H_{32}EuF_9N_2O_6 \cdot 1/2C_3H_8O$	$C_{52}H_{32}EuF_9N_2O_6$
Formula weight	1133.80	1103.76
Crystal size (mm)	0.45×0.40×0.04	0.45×0.32×0.25
Crystal system	Orthorhombic	Monoclinic
Volume (Å^3)	10071.1(3)	4717(2)
Density (calc.) (mg m^{-3})	1.496	1.554
Space group	Pna2$_1$	P2$_1$/c
Unit cell dimensions	a=20.8160(4) Å	a=11.292(3) Å
	α=90°	α=90°
	b=11.1787(2) Å	b=23.465(5) Å
	β=90°	β=97.153(12)°
	c=43.2801 Å	c=17.940(4) Å
	γ=90°	γ=90°
Z	8	4
Absorption coefficient (mm^{-1})	1.331	1.418
F(000)	4536	2200
θ range for data collection (°)	0.94–25.06	2.01–25.02
Reflections collected	44 652	8750
Independent reflections	13 301 (R_{int}=0.0496)	8302 (R_{int}=0.0607)
Refinement method	Full-matrix least-squares on F^2	
R indices [$I>2\sigma(I)$]	$R1$=0.0626	$R1$=0.0600
	$wR2$=0.1333	$wR2$=0.1114
R indices (all data)	$R1$=0.1085	$R1$=0.1297
	$wR2$=0.1564	$wR2$=0.1633
Goodness of fit on F^2	1.004	1.043

Table 2
Selected bond lengths (Å)

Bond	Blocks	Plates (Eu1)	Plates (Eu1A)
Eu–O1	2.344(5)	2.373(9)	2.329(9)
Eu–O2	2.356(6)	2.352(11)	2.435(10)
Eu–O3	2.371(5)	2.320(9)	2.371(8)
Eu–O4	2.359(6)	2.372(10)	2.287(12)
Eu–O5	2.336(6)	2.371(8)	2.382(9)
Eu–O6	2.387(5)	2.363(11)	2.372(10)
Eu–N1	2.598(6)	2.57(2)	2.582(13)
Eu–N2	2.570(7)	2.552(12)	2.558(12)

and a sample of the plates obtained from this separation were then subjected to structure determination by X-ray diffraction and the crystal data are presented in Table 1, and the Eu–O and Eu–N bond distances are listed in Table 2. (X-ray diffraction on the blocks obtained in the separation demonstrated that they have the same structure as those from benzene/hexane.) The blocks contain a single eight-coordinate geometry for the complex, whereas the plates contain two crystallographically independent complexes that are related by a pseudo inversion center. The structures are shown in Figs. 3 and 4.

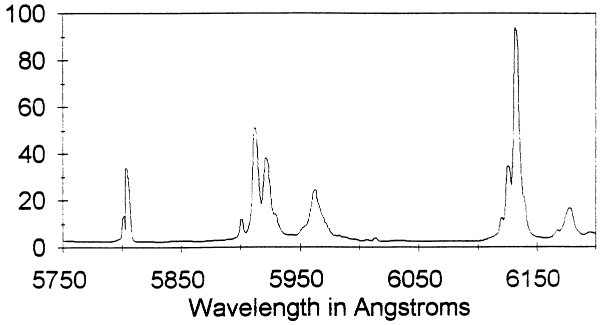

Fig. 2. Luminescence spectrum of the plates.

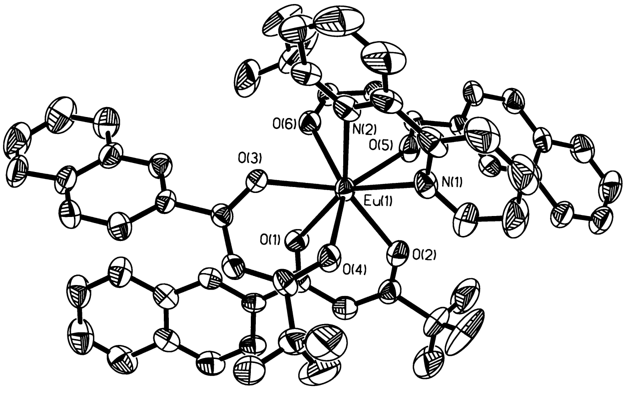

Fig. 3. Molecular structure of Eu(TAN)$_3$·dipy in the blocks.

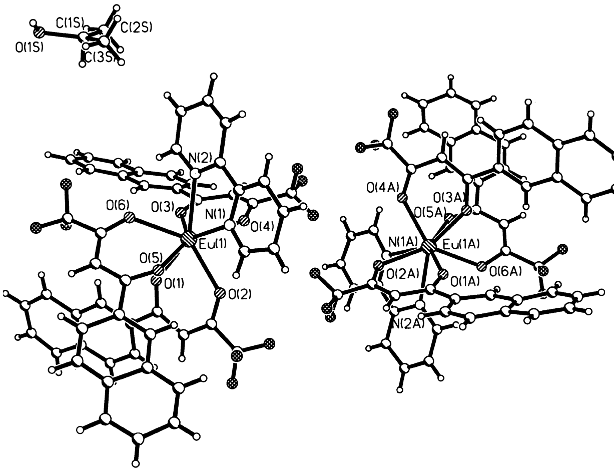

Fig. 4. Molecular structure of the two Eu(TAN)$_3$·dipy molecules in the plates.

4. Discussion

The compound Eu(TAN)$_3$·dipy is similar to other adducts of the rare earth tris-β-diketonates. As expected, it has a relatively low melting point, solubility in a number of organic solvents of reasonably low polarity and, because of the presence of the trifluoromethyl and 2-naphthyl substituents, is strongly luminescent under excitation in the ultraviolet region. (The luminescence can also be observed in sunlight filtered through the laboratory windows.) The spectra in Figs. 1 and 2 are typical of eight-coordinate chelates but because of the very low symmetry of the complex, cannot be used to determine the geometry around the europium(III) ion. They are, however, distinctive and distinguish one preparation from another.

The most interesting feature of the complex is the fact that recrystallization results in substances that have different luminescence spectra which is indicative of different sites for the europium(III) ion. The structures of the complexes in the two different crystals are different and they are isomers in the sense that the geometries of the coordination polyhedra are different. In gross features the two forms are very similar and the bond distances (Table 2) for the two complexes in the plates and the one in the blocks are in the general range found for adducts of the tris-β-diketonates [1]. As is usual in the case of eight-coordination, the basic coordination polyhedra can be examined in a number of ways. The usual visual presentation of eight-coordinate structures is given in a way that suggests the polyhedron is the square antiprism even though other polyhedra are possible. It is generally agreed that the determination of the best polyhedron is by means of the method proposed by Porai-Koshits and Aslanov [7]. For Eu(TAN)$_3$·dipy this analysis suggests that the two structures present in the plates are both well-defined square antiprisms with the square faces defined by O1–O2–O3–O4 and O5–O6–N1–N2. The coordination polyhedron of the europium(III) ion in the blocks is more irregular but can be described as a bicapped trigonal prism. In this polyhedron the triangular faces are O1–O2–O4 and O6–O5–N2 and the capping atoms are O_3 and N_1. Consequently, it can be seen that the two crystalline forms of $Eu(TAN)_3 \cdot dipy$ are different from one another and are the second example of structural isomers due to the different coordination polyhedra that are adopted.

Because there are presently only two such examples, the factors that are operative in determining the formation of structural isomers of this type are not clear and additional complexes will be needed. Studies are in progress that will hopefully allow these to be determined.

Acknowledgements

This work was supported by the Undergraduate Research Opportunities Program and the Graduate School of the University of Minnesota.

References

[1] D. Moser, M.S. Thesis, University of Minnesota, 1996.

[2] M.L. Nakamura, R. Nakamura, K. Nagai, M. Shiemi, S. Tomada, Y. Takeuchi, A. Ouchi, Bull. Chem. Soc. Jpn. 59 (1986) 332.

[3] R.C. Holz, L.C. Thompson, Inorg. Chem. 32 (1993) 5251.

[4] O.L. Raven, M.S. Thesis, University of Minnesota, 1991.

[5] M.A. Porai-Koshits, L.A. Aslanov, Zhur. Strukt. Khim. 13 (1972) 266.

[6] N.K. Ito, M.S. Thesis, University of Minnesota, 1994.

[7] E.L. Muetterties, L.J. Guggenberger, J. Am. Chem. Soc. 96 (1974) 1748.