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Structures of the 1,10-phenanthroline and 2,2′-dipyridyl adducts of tris(2,6-dimethylheptane-3,5-dionato)europium(III)

D.F. Moser[a], L.C. Thompson[a,*], V.G. Young Jr.[b]

[a]Department of Chemistry, University of Minnesota, Duluth, MN 55803, USA

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

Abstract

The title compounds, conveniently abbreviated Eu(DMH)$_3$·o-phen and Eu(DMH)$_3$·dipy, have been prepared and characterized by means of their luminescence spectra and by complete structure determination by X-ray diffraction. The spectral results indicated the existence of two europium sites in the dipy compound but only one in the o-phen complex. The X-ray results show that the o-phen complex has a single geometry, the coordination polyhedron of which is best approximated as a square antiprism, whereas there are two geometries in the dipy complex, both of which are also square antiprisms but are more distorted. In all cases the chelate rings span the s edges of the square antiprism and the bond distances are typical for this type of complex.

Keywords: Eu(DMH)$_3$·dipy; Eu(DMH)$_3$·o-phen; Luminescence spectroscopy; X-Ray diffraction

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1. Introduction

One of the most widely-studied group of complexes of the rare earth ions has been the beta-diketones. Many tris- and tetrakis complexes have been prepared as well as many adducts of the tris-complexes in which the fourth ligand has been a monodentate, bidentate, or even terdentate ligand. Although there was an intense period of activity in the early 1960s, particularly into the luminescence properties of the europium and terbium complexes, much of this work was of marginal quality and it is now quite evident that the assignment of the coordination geometry on the basis of the luminescence spectrum is not in general feasible in these compounds because of the very low symmetry [1].

With the 1969 discovery of the ability of europium beta-diketonates to function as shift reagents in NMR spectroscopy [2], there was a renewed interest in these adducts and a number of structures were determined by X-ray diffraction. These studies were important in beginning to understand the factors that influence the coordination polyhedron that is adopted by seven- and eight-coordinate rare earth complexes. Our interest in these complexes was rekindled by the report that two slightly different geometric arrangements are present in Eu(DPM)$_3$·2DMF (DPM=dipivaloylmethane) [3] as evidenced both by luminescence studies and an X-ray structure determination. Our initial studies were with Eu(DPM)$_3$·terpy [4] (which contains two slightly different polyhedra) and Eu(DPM)$_3$·DMOP (DMOP=2,9-dimethyl-1,10-phenanthroline) [5] (which contains two very different arrangements of the chelate rings). Subsequently, we were able to prepare individual crystals of two isomers of Eu(tfa)$_3$·2H$_2$O (tfa=1,1,1-trifluoroacetylacetone) [6] (one is a bicapped trigonal prism and one is a dodecahedron) and two isomers of Eu(TAN)$_3$·dipy (TAN=4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedione) [7] (one isomer is a bicapped trigonal prism and the other contains two slightly different square antiprisms).

We have continued our studies of this type of complex by varying the beta-diketone while using TPPO, dipy, o-phen, and terpy as the adduct molecules. In this paper we report the results of the luminescence and structural studies of the two compounds Eu(DMH)$_3$·dipy and Eu(DMH)$_3$·o-phen in which the symmetrical beta-diketone has two iso-propyl substituents.

2. Experimental

The two compounds were prepared by the same method. To 5 ml of hot ethanol were added 3 mmols of DMH

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*Corresponding author.

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(Eastman) and 3 mmols of NaOH. After the solution was complete, 1 mmol of the neutral ligand (dipy or o-phen; Aldrich Chemical Company) was added and the solution was stirred for approximately 10 mins. Then 1 mmol of a solution of $EuCl_3$ (prepared from HCl and Eu_2O_3; Research Chemicals) was added at the rate of 1 drop/min with stirring. A precipitate formed immediately and after complete addition of the $EuCl_3$, the mixture was stirred for an additional hour. The precipitate was filtered, washed with absolute alcohol and dried under vacuum. Crystals suitable for X-ray diffraction were obtained by recrystallization from absolute ethanol ($Eu(DMH)_3$·dipy) or acetonitrile ($Eu(DMH)_3$·o-phen). Microanalysis was performed by Desert Analytics. Calc. (Exp.): $Eu(DMH)_3$·dipy (m.p. 147–149°C); C, 57.43 (57.10); H, 6.90 (6.74); N, 3.62 (3.56); $Eu(DMH)_3$·o-phen (m.p. 181–183°C); C, 58.71 (59.04); H, 6.70 (6.74); N, 3.51 (3.50).

Luminescence spectra were obtained with a McPherson RS-10 spectrophotometer at 77 K using 365 nm excitation from a Hg lamp as previously described [5]. A single crystal of each compound was attached to a glass fiber and data were collected at 298(2) K with the Siemans SMART system using Mo–Ka radiation. An initial set of cell constants was calculated from reflections harvested from three sets of 20–30 frames. These initial sets of frames are oriented such that orthogonal wedges of reciprocal space were surveyed. All calculations were performed with the SHELXTL v. 5.0 suite of programs. Refinements with SELXTL-Plus were performed with F^2 rather than F which enables all data to be used.

3. Results

The elemental analyses indicated that the desired adducts had been successfully synthesized and that each contained one molecule of either dipy or o-phen. The melting point of the dipy adduct is about 35°C lower than that of the o-phen adduct which is typical for these types of compounds. Both compounds give a strong red luminescence (Figs. 1 and 2) when excited in the ultraviolet and emission is observed from both the $^5D_0$ and $^5D_1$ levels to the various ^7F levels of the ground state. The $^5D_0 \rightarrow {}^7F_0$ transition in the o-phen adduct occurs at 580.2 nm and is accompanied by a weaker shoulder at 579.2 nm. Although this might indicate the existence of two europium sites, the very large energy difference of 30 cm^{-1} suggests that this second band is due to a vibronic transition or perhaps to a minor impurity. The occurrence of three transitions in the $^5D_0 \rightarrow {}^7F_1$ region and five transitions in the $^5D_0 \rightarrow {}^7F_2$ region supports the existence of only a single europium site. The dipy complex has two distinct transitions in the $^5D_0 \rightarrow {}^7F_0$ region at 579.95 and 580.3 nm as well as a small shoulder at 579.55 nm. From the arguments above, this suggests that there are two sites for the europium and the observation of four peaks, two of which have shoulders, in the $^5D_0 \rightarrow {}^7F_1$ region and of five peaks, all of which have shoulders, in the $^5D_0 \rightarrow {}^7F_2$ region lend support to this conclusion. Although our experience suggests the validity of these conclusions, it was necessary to solve the structure of the compounds in order to be certain.

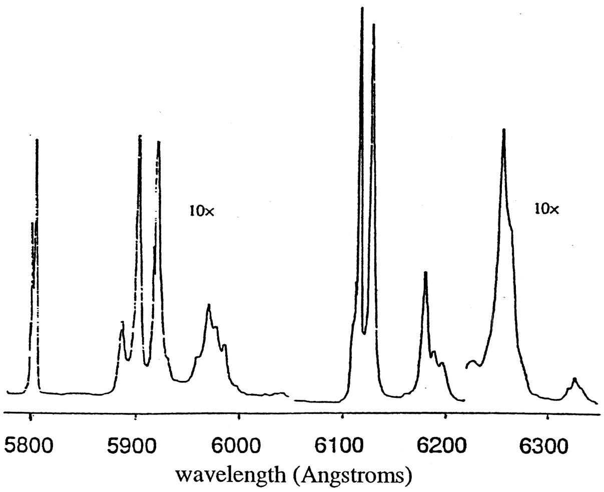

Fig. 1. Luminescence spectrum of $Eu(DMH)_3$·dipy.

Single crystals of the two compounds were studied by X-ray diffraction and the structures were successfully determined. The crystal data are given in Table 1 and the Eu–O and Eu–N distances are given in Table 2. As indicated by the luminescence data, the o-phen complex contains a single geometry around the europium whereas in the dipy adduct there are two distinct europium centers. The structures of the two adducts are shown in Figs. 3–5.

4. Discussion

The two adducts reported here are typical of this type of compound. They have relatively low melting points,

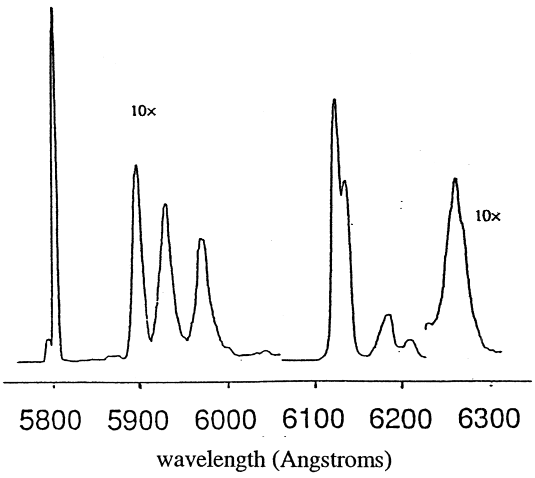

Fig. 2. Luminescence spectrum of $Eu(DMH)_3$·o-phen.

Table 1
Crystal data and structure refinement

Empirical formula	$C_{39}H_{53}EuN_2O_6$	$C_{37}H_{53}EuN_2O_6$
Formula weight	797.79	773.77
Crystal size (mm)	0.55×0.45×0.30	0.35×0.30×0.15
Crystal system	Monoclinic	Triclinic
Volume (Å^3)	8044.50(8)	4054.9(1)
Density (calc. Mg/m^3)	1.317	1.267
Space group	$C2/c$	$P\bar{1}$
Unit cell dimensions	a=31.1243(2) Å	13.3394(2) Å
	b=18.27350(10) Å	16.8685(2) Å
	c=16.60880(10) Å	18.1199(3) Å
	α=90°	92.153(1)°
	β=121.6130(10)°	94.910(1)°
	γ=90°	92.513(1)°
Z	8	4
Absorption coefficient (mm^{-1})	1.603	1.587
$F(000)$	3296	1600
θ range for data collection (°)	1.35 to 25.06	1.13 to 25.05
Reflections collected	19146	20012
Independent reflections	7027 (R_{int}=0.0343)	1321 (R_{int}=0.0329)
Refinement method	Full-matrix least squares on F^2	Full-matrix squares on F^2
R indices [$I>2F(I)$]	R1=0.0583, wR2=0.1650	R1=0.0427, wR2=0.1014
R indices (all data)	R1=0.0754, wR2=0.1815	R1=0.0526, wR2=0.1118
Goodness of fit on F^2	1.108	1.136

solubility in a number of organic solvents, and exhibit a strong luminescence when excited with near-ultraviolet light. The overall symmetry of the complexes is too low to allow a determination of the geometry around the europium ion but the spectra are distinctive and can be used to identify the compounds. Although the o-phen adduct has a single europium geometry as determined by X-ray diffraction, the dipy adduct has two geometries which are distinct, but very similar. This existence of more than one coordination site for the lanthanide ion was mentioned earlier and is also found in other eight-coordinate rare earth complexes. For example, the tetrakis-pyridinethiolates have recently been shown to have three inequivalent coordination geometries in the unit cell [8]. The best description of the coordination polyhedra was determined by the method advanced by Porai-Koshits and Aslanov [9] and the calculated angles are given in Table 3. For each of the three complexes the calculated angles for the coordination polyhedron are in substantial agreement with those of the square antiprism although it is clear that the agreement is better for the o-phen adduct and that the dipy polyhedra are more distorted. This analysis indicates that each chelate ring spans an s edge of the antiprism. This same arrangement is found for $Eu(DPM)_3$·o-phen

Table 2
Selected bond lengths (Å)

Bond	$Eu(DMH)_3$·o-phen	$Eu(DMH)_3$·dipy[a]	
		Eu(1A)	Eu(1E)
Eu–O(1B)	2.342	O(2C) 2.353	O(1F) 2.388
Eu–O(2B)	2.363	O(1C) 2.400	O(2F) 2.345
Eu–O(2C)	2.334	O(1D) 2.367	O(2H) 2.358
Eu–O(1C)	2.341	O(2D) 2.344	O(1H) 2.347
Eu–O(1D)	2.348	O(2B) 2.349	O(1G) 2.331
Eu–O(2D)	2.364	O(1B) 2.353	O(2G) 2.346
Eu–N(2A)	2.617	N(1A) 2.631	N(2E) 2.641
Eu–N(1A)	2.622	N(2A) 2.636	N(1E) 2.624
Eu–O (ave.)	2.349	2.361	2.352
Eu–N (ave.)	2.620	2.634	2.633

[a] The ligand atoms are listed so that they correspond to the same positions in the coordination polyhedra. The first four values define the upper square in a clockwise direction and the second four define the lower square in a counterclockwise direction.

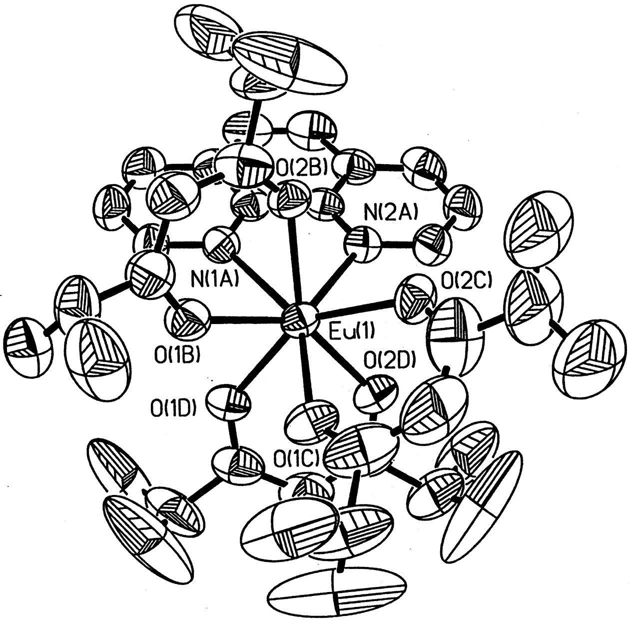

Fig. 3. Structure of $Eu(DMH)_3$·o-phen.

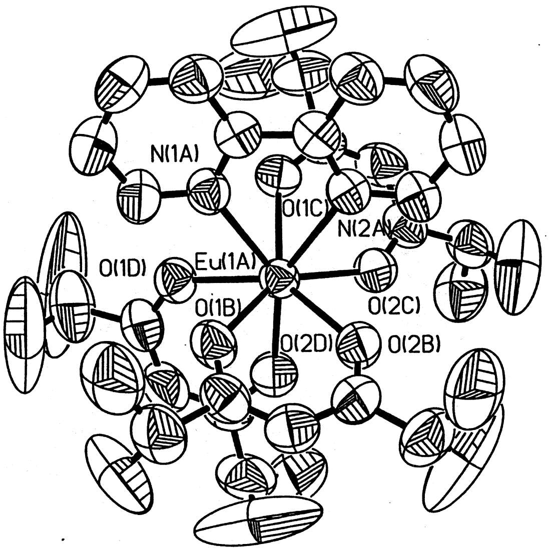

Fig. 4. Structure of Eu(DMH)$_3$·dipy (Eu1A).

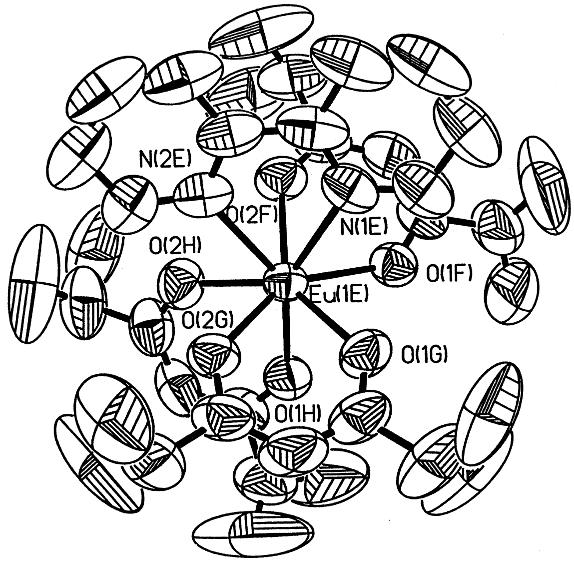

Fig. 5. Structure of Eu(DMH)$_3$·dipy (Eu1E).

Table 3
Angles to define the polyhedron

	$\delta 1$	$\delta 2$	$\delta 3$	$\delta 4$	$\phi 1$	$\phi 2$
Ideal square antiprism	0.0	0.0	52.4	52.4	24.5	24.5
Eu(DMH)$_3$·o-phen	3.9	3.0	53.7	53.0	25.0	25.0
Eu(1A)(DMH)$_3$·dipy	2.8	8.4	49.7	49.6	21.6	23.5
Eu(1E)(DMH)$_3$·dipy	8.2	6.8	48.8	53.5	21.5	26.4

[10] which also has a single polyhedron and in which the beta-diketone has two *t*-butyl groups rather than two isopropyl groups as in DMH. In the DPM complex the deviation from the square antiprism is slightly more pronounced as well. This arrangement of the chelate rings is in contrast to the observation that in the two geometries found for Eu(DPM)$_3$·DMOP one has all four rings spanning l edges and the other has two spanning l edges and two spanning s edges. Moreover, the deviation from the square antiprism is also larger.

Our ultimate aim is to try to identify those factors that are instrumental in determining the choice of coordination polyhedron, the existence of more than one geometry in a crystal, and in allowing separate isomers to be isolated for these eight-coordinate complexes. Although it is clear that crystal forces must play an important role in these effects, at the present this is still an elusive goal. For example, the existence of separate isomers for Eu(TAN)$_3$·dipy, and of two geometries in one of them, might suggest that the more flexible dipy favors the formation of adducts with multiple sites. However, both Eu(BTA)$_3$·dipy (BTA= benzoyltrifluoroacetone) and Eu(TMH)$_3$·dipy (TMH= 1,1,1-trifluoro-5-methyl-2,4-hexandione) have a single approximately square antiprismatic site. A number of additional adducts of this type have been characterized in our laboratory, but these factors have yet to be unraveled.

Acknowledgements

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