ELSEVIER

Journal of Alloys and Compounds 323–324 (2001) 177–180

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Structure and emission spectrum of the *o*-phenanthroline adduct of *tris*(6-methyl-2,4-heptanedionato)europium(III)

L.C. Thompson*, S. Berry

Department of Chemistry, University of Minnesota, Duluth, Duluth, MN 55812, USA

Abstract

The title compound, conveniently abbreviated Eu(MHD)$_3$·*o*-phen, has been prepared and characterized by means of its luminescence spectrum and by complete structure determination by X-ray diffraction. The β-diketone ligand is unsymmetrical with a methyl group at one end and an iso-butyl group at the other. Monoclinic crystals having m.p. 186–187°C were isolated from dichloromethane/iso-propanol. The luminescence spectrum is typical for low-symmetry complexes of this type with a single sharp $^5D_0 \rightarrow {}^7F_0$ transition at 579.9 nm accompanied by a weak shoulder. The $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions are completely resolved with weak additional transitions that are most likely vibronic in origin. The X-ray structure shows a single eight-coordinate coordination geometry that approximates a square antiprism. The average Eu–O and Eu–N distances are 2.358 and 2.628 Å and are typical. Our initial assumption that the unsymmetrical β-diketone would lead to multiple sites was not substantiated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Eu(MHD)$_3$·*o*-phen; Luminescence spectroscopy; X-ray diffraction

1. Introduction

The β-diketone complexes of the rare earths have been widely studied during the past 40 years. Of particular interest have been the adducts of the *tris* complexes in which the donor atom of the adduct molecule is oxygen or nitrogen. The early impetus for the study of these complexes came from the luminescent properties of europium(III) and terbium(III) and from the application of the europium complexes with DPM and fod (DPM = dipivaloylmethane; fod = 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione) as shift reagents in NMR spectroscopy [1]. More recently the adducts have found applications as potential precursors for various mixed metal oxides [2] and as radiation dosimeters for ultraviolet light [3].

The structures of a few of these adducts were determined as part of the studies directed at determining the nature of the interaction leading to their application as shift reagents. Depending on the ligand, seven, eight, or nine-coordinate adducts may be formed. These compounds are generally easily prepared, quite stable in air, and are easily handled although we now realize that many of the preparations in the past often resulted in impure mixtures [1]. The observation that Eu(DPM)$_3$·2DMF (DMF = dimethylformamide) had two slightly different geometrical arrangements around the europium(III) ions [4] rekindled our interest in these compounds and the use of luminescence spectra to determine the number of different sites. Because the complexes have low symmetry, it is generally not possible to determine the symmetry of the sites as the degeneracy is completely removed. However, the number of sites can be determined from the $^5D_0 \rightarrow {}^7F_0$ transition and the spectra are usually very characteristic for a particular compound.

Our initial studies were with Eu(DPM)$_3$·terpy (terpy = 2,2′:6′,2″-terpyridine) (a nine-coordinate molecule with two slightly inequivalent coordination polyhedra) [5] and Eu(DPM)$_3$·DMOP (DMOP = 2,9-dimethyl-1,10-phenanthroline) (an eight-coordinate molecule that contains two very different polyhedra) [6]. Interestingly, one of the europium(III) ions in the bridged dimer of Eu(DPM)$_3$·triglyme (triglyme = 1,2-*bis*(2-methoxyethoxy)ethane) has two different polyhedra as well [2]. The ready availability of this class of compounds led us to consider that it might be possible to prepare two types of crystals for a single compound in which the coordination polyhedra were different and could be considered as isomers. Subsequently this has been accomplished for the eight coordinate molecules Eu(tfa)$_3$·2H$_2$O (tfa = 1,1,1-trifluoro-2,4-pentanedione) (one is a bicapped trigonal prism and one is a

---

*Corresponding author. Tel.: +1-218-726-8716; fax: +1-218-726-7394.

E-mail address: lthompso@d.umn.edu (L.C. Thompson).

PII: S0925-8388(01)01124-0

dodecahedron) [7] and $Eu(TAN)_3 \cdot dipy$ (TAN = 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedione; dipy = 2,2′-bipyridine) (one isomer is a bicapped trigonal prism and the other contains two slightly different square antiprisms) [8]. Moreover, we now have also prepared four different forms of $Eu(DBM)_3 \cdot TPPO$ (DBM = 1,3-diphenyl-1,3-propanedione; TPPO = triphenylphosphine oxide) [9], one of which had been reported previously [10].

The lanthanide ions are relatively large and can adopt a variety of geometrical shapes for a given coordination number. The adoption of two (or more) coordination polyhedra in a single crystal is not particularly surprising and is customarily attributed to packing effects although it is rare to be able to discern these in any detail. We have been interested in trying to see what role, if any, the substituents on the β-diketone play. In this communication we have prepared and characterized the *o*-phenanthroline adduct of an unsymmetrical β-diketone which has a small methyl group on one end and a bulkier iso-propyl group on the other.

2. Experimental

The compound was prepared in the usual way [11]. To 5 ml of hot ethanol were added 3 mmols of MHD (Pfaltz and Bauer) and 3 mmols of NaOH. After solution was complete, 1 mmol of *o*-phen (Aldrich) was added and the solution was stirred for approximately 10 min. Then an aqueous solution of 1 mmol of $EuCl_3$ (prepared from HCl and Eu_2O_3; Research Chemicals) was added at the rate of 1 drop per minute 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 ethanol, and dried under vacuum. Crystals suitable for X-ray diffraction were obtained by recrystallization from dichloromethane/isopropanol. Microanalysis was performed by Desert Analytics. Calc. (Exp.): $Eu(MHD)_3 \cdot o$-phen (m.p. 186–189°C); C 57.21 (56.89); H 6.27 (6.34); N 3.71 (3.66)).

The luminescence spectrum was obtained with a McPherson RS-10 spectrophotometer from a crystalline sample that was placed in a quartz tube and immersed in liquid nitrogen. The excitation source was the 365 nm line from a mercury lamp and was selected by a glass filter. The slits were set for an instrument resolution of 0.1 nm. A single crystal was attached to a glass fiber and diffraction data were collected at 297(1)K on an Enraf–Nonius CAD-4 diffractometer with graphite monochromated Mo–K_α radiation. The structure was solved by direct methods using the TEXSAN crystallographic software package of Molecular Structure Corporation. The isopropyl group on molecule A was disordered and atom C6(A) was replaced by two fractional atoms, C6(1A) and C6(2A). Atom C6(1A) had 57(3) occupancy.

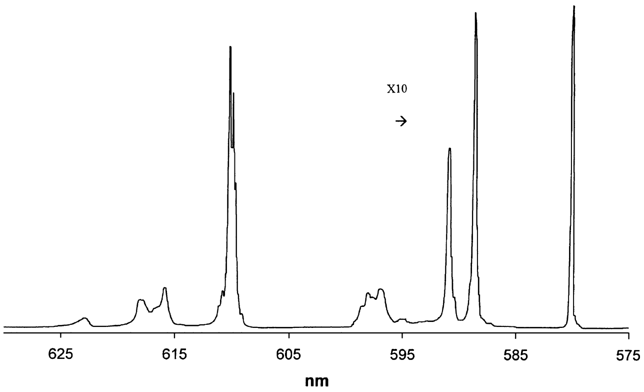

Fig. 1. Luminescence spectrum of $Eu(MHD)_3 \cdot o$-phen.

3. Results

The elemental analysis confirmed that the desired compound had been synthesized and that the adduct contained one molecule of *o*-phen and was not solvated. The compound gave an intense red emission as expected when excited in the near-ultraviolet. The emission originates mainly on the $^5D_0$ level and the strongest transitions are to $^7F_{0,1,2}$. The $^5D_0 \rightarrow {}^7F_0$ transition occurs at 579.9 nm and has a very weak shoulder which is most likely vibronic in origin. There are two sharp peaks and a weaker broad peak in the region characteristic of the $^5D_0 \rightarrow {}^7F_1$ transition and there is one sharp peak resolved into at least three components as well as two broader peaks in the $^5D_0 \rightarrow {}^7F_2$ region. In addition there are a number of weaker features that may well be vibronic in origin. These spectral features are very characteristic of this type of compound and illustrate the difficulty of relying solely on the luminescence spectrum for the characterization of the coordination geometry. The existence of a single line in the $^5D_0 \rightarrow {}^7F_0$ region is perhaps the best indicator, but even this can occasionally lead one astray (Fig. 1).

The structure was successfully determined by X-ray diffraction and the existence of a single eight-coordinate molecule was confirmed. The crystal data are given in Table 1 and the Eu–O and Eu–N distances along with the relevant angles are given in Table 2. The structure is illustrated in Fig. 2.

4. Discussion

The compound, $Eu(MHD)_3 \cdot o$-phen, is quite characteristic of this type of rare earth adduct. It has a relatively low melting point, solubility in a number of organic solvents, and is strongly luminescent when excited with near-ultraviolet light. The symmetry of the compound is low and, as a result, it is not possible to determine the molecular geometry from the luminescence spectrum, although the spectrum is characteristic for the compound. The structure determined by X-ray diffraction shows that the molecule

Table 1
Crystal data and structure refinement

Empirical formula	$EuC_{36}N_2H_{47}O_6$
Formula weight	755.74
Crystal size (mm)	0.450×0.150×0.150
Crystal system	Monoclinic
Volume ($Å^3$)	3690(5)
Density (calc. g/cm^3)	1.360
Space group	$P2_1/n$ (#14)
Unit cell dimensions	$a = 9.822(6)$ Å $b = 24.592(6)$ Å $c = 15.277(6)$ Å $\beta = 90.38(4)°$
Z	4
$F(000)$	1552
Scan type	ω
$2\theta_{max}$	47.9°
Reflections collected	6735
Unique reflections	5935 ($R_{int} = 0.038$)
No. observations ($I > 2.00\sigma(I)$)	3903
Refinement method	Full-matrix least squares
Function minimized	$\Sigma\omega(\|F_0\| - \|F_c\|)^2$
Residuals: R_1, R_w	0.040, 0.043
Goodness of fit indicator	1.35

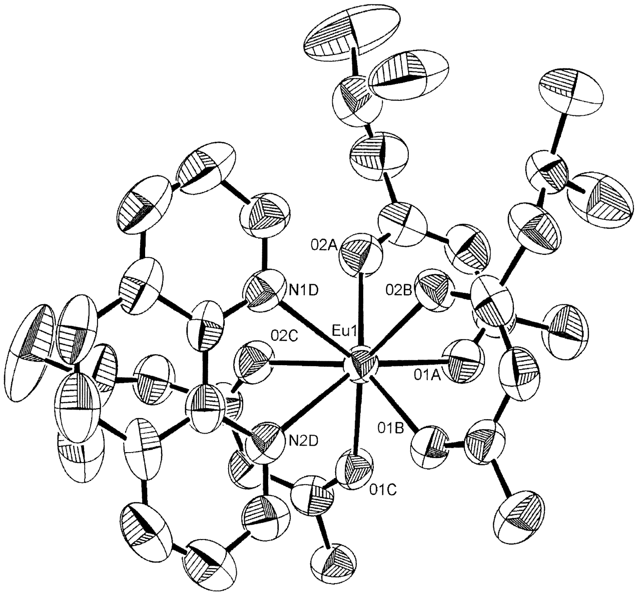

Fig. 2. Structure of Eu(MHD)$_3$·*o*-phen.

contains the europium(III) ion in a single eight-coordinate environment. The best description of the coordination polyhedron was determined by the method of Porai-Koshits and Aslanov [12] and the calculated angles are given in Table 3. The values selected are clearly in good agreement with those expected for the square antiprism and the two square faces are formed by O(2B)–N(1D)–N(2D)–O(1B) and O(2A)–O(2C)–O(1C)–O(1A). The four chelate rings span the *s* edges of the antiprism in much the same way as in Eu(DMH)$_3$·*o*-phen and Eu(DMH)$_3$·dipy (DMH = 2,6-dimethylheptane-3,5-dione) [11]. In the similar compounds, Eu(DPM)$_3$·DMOP [6] and Eu(DPM)$_3$·*o*-phen [13], in which the substituents are only slightly bulkier (*t*-butyl versus iso-propyl or iso-butyl), two rings span the *s* edges and two span the *l* edges. Whether this is a consequence of the bulky groups will have to await the structures of additional examples.

Our ultimate goal is to determine those factors that influence the formation of compounds with multiple coordination sites for the central metal ion as well as those factors that lead to the isolation of distinct geometric isomers. Although at present we have studied and characterized some twenty eight-coordinate complexes of this type, it is still not possible to predict when such multiple sites or separate compounds will be formed. All of the *o*-phen adducts that have been structurally characterized have only a single coordination polyhedron. On the other hand, several of the dipy adducts have two coordination polyhedra and in the case of Eu(TAN)$_3$·dipy, there are two different isolable complexes and one of these has two sites [8]. Lest it be assumed that a flexible adduct molecule is

Table 2
Selected bond lengths (Å) and angles (deg)

Eu(1)–O(1A)	2.364(5)	Eu(1)–O(2B)	2.348(5)
Eu(1)–O(1B)	2.354(5)	Eu(1)–O(2C)	2.370(5)
Eu(1)–O(1C)	2.349(5)	Eu(1)–N(1D)	2.610(6)
Eu(1)–O(2A)	2.366(6)	Eu(1)–N(2D)	2.647(6)
O(1A)–Eu(1)–O(1B)	84.3(2)	O(1C)–Eu(1)–O(2B)	145.7(2)
O(1A)–Eu(1)–O(1C)	76.4(2)	O(1C)–Eu(1)–O(2C)	72.0(2)
O(1A)–Eu(1)–O(2A)	72.2(2)	O(1C)–Eu(1)–N(1D)	133.3(2)
O(1A)–Eu(1)–O(2B)	81.5(2)	O(1C)–Eu(1)–N(2D)	79.4(2)
O(1A)–Eu(1)–O(2C)	115.2(2)	O(2A)–Eu(1)–O(2B)	79.7(2)
O(1A)–Eu(1)–N(1D)	147.9(2)	O(2A)–Eu(1)–O(2C)	74.2(2)
O(1A)–Eu(1)–N(2D)	149.0(2)	O(2A)–Eu(1)–N(1D)	81.2(2)
O(1B)–Eu(1)–O(1C)	79.3(2)	O(2A)–Eu(1)–N(2D)	137.2(2)
O(1B)–Eu(1)–O(2A)	146.0(2)	O(2B)–Eu(1)–O(2C)	141.9(2)
O(1B)–Eu(1)–O(2B)	72.7(2)	O(2B)–Eu(1)–N(1D)	76.2(2)
O(1B)–Eu(1)–O(2C)	139.4(2)	O(2B)–Eu(1)–N(2D)	109.5(2)
O(1B)–Eu(1)–N(1D)	110.2(2)	O(2C)–Eu(1)–N(1D)	72.8(2)
O(1B)–Eu(1)–N(2D)	72.4(2)	O(2C)–Eu(1)–N(2D)	74.4(2)
O(1C)–Eu(1)–O(2A)	116.9(2)	N(1D)–Eu(1)–N(2D)	62.1(2)

Table 3
Angles to define the polyhedron

Ideal square antiprism	0.0	0.0	52.4	52.4	24.5	24.5
Ideal dodecahedron	29.5	29.5	29.5	29.5	0.0	0.0
Ideal bicapped trigonal prism	21.8	0.0	48.2	48.2	14.1	14.1
$Eu(MHD)_3 \cdot o$-phen	1.8	2.1	50.8	52.9	27.3	23.3

necessary for the formation of these isomers, it is well to be reminded that two very different sites exist in $Eu(DPM)_3 \cdot DMOP$ which contains a very rigid adduct molecule [6].

The β-diketone, MHD, is unsymmetrical and does not lead to a compound with multiple sites at least under the crystallization conditions employed here. We are continuing to study these β-diketone adducts with the hope that the critical factors will be discovered.

Acknowledgements

This work was supported by the American Chemical Society-Petroleum Research Fund. The X-ray structure was carried out by Professor Doyle Britton of the University of Minnesota, Twin Cities.

References

[1] L.C. Thompson, Complexes, in: K. Gschneidner, L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, Vol. 3, North-Holland, Amsterdam, 1979.
[2] S.R. Drake, A. Lyons, D.J. Otway, A.M.Z. Slawin, D.J. Williams, J. Chem. Soc., Dalton Trans. (1993) 2379.
[3] P. Santa Cruz Oliveira, communication.
[4] J.A. Cunningham, R.E. Sievers, Inorg. Chem. 19 (1980) 595.
[5] R.C. Holz, L.C. Thompson, Inorg. Chem. 27 (1988) 4640.
[6] R.C. Holz, L.C. Thompson, Inorg. Chem. 32 (1993) 5251.
[7] O.L. Raven, M.S. Thesis, University of Minnesota, 1991.
[8] L.C. Thompson, F.W. Atchison, V.G. Young Jr., J. Alloys Comp. 265–268 (1998) 765.
[9] F.W. Atchison, unpublished.
[10] M.-Z. Wang, L.-P. Jin, S.-X. Liu, G.-L. Cai, J.-L. Huang, W.-P. Qin, S.-H. Huang, Sci. China (Series B) 37 (1994) 410.
[11] D.F. Moser, L.C. Thompson, V.G. Young Jr., J. Alloys Comp. 303–304 (2000) 121.
[12] M.A. Porai-Koshits, L.A. Aslanov, Zhur. Strukt. Khim. 13 (1972) 266.
[13] N.K. Nao, M.S. Thesis, University of Minnesota, 1994.