

Synthesis and luminescent properties of Eu^{3+} -complexes with 2-acyl-1,3-indandionates (ACIND) and TPPO ligands: The first X-ray structure of Eu–ACIND complex

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Abstract

Europium complexes presenting general formulas $[\text{Eu}(\text{ACIND})_3(\text{H}_2\text{O})_2]$ and $[\text{Eu}(\text{ACIND})_3(\text{TPPO})_2]$ have been synthesized and characterized. In these formulas ACIND stands for the ligands 2-acetyl-1,3-indandionate (AIND), 2-isovaleryl-1,3-indandionate (ISOVIND) or 2-benzyl-1,3-indandionate (BIND). The $[\text{Eu}(\text{ISOVIND})_3(\text{H}_2\text{O})(\text{EtOH})]$ complex was also prepared and its structure determined by single crystal X-ray analysis, showing that this complex crystallizes in a monoclinic space group $P2_1/n$ with the water molecules bridging through the hydrogen bond. The Eu(III) ion is eight-coordinate in a bicapped trigonal prismatic geometry defined by the oxygen donor atoms with a site of symmetry close to C_{2v} . Isovaleryl groups in the ISOVIND molecules in the structure are disordered over two positions of the europium complex. Carbon atoms in ethanol molecule are disordered by the thermal vibration. Photoluminescence properties of these complexes in solid state were investigated both experimentally and theoretically, suggesting an efficient ligand-to-metal intramolecular energy transfer process.

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1. Introduction

There is a great interest in the study and development of new trivalent rare earth complexes (RE^{3+}) that present strong luminescence for application such as selective luminescent probes of biological structures [1], fluoroimmunoassay agents [2] and organic electroluminescent devices (OLEDs) [3,4].

A particular attention has been given to the studies of complexes containing β -diketonates as ligands. This kind

of ligand has been successfully employed as “antenna” [5]. In order to increase the europium luminescence intensity in the diketonate complexes a second kind of unidentate or bidentate ligands such as sulfoxide, heterocyclic, or phosphine oxides are usually bonded to europium ion [5]. These ligands coordinated to lanthanide ions, substituting organic solvent or water molecules that act as luminescence quencher for this metal ion. Among these ligands triphenylphosphine oxide (TPPO) has been the focus of some studies in the literature [4]. When coordinated to the metal ion substituting the water molecules TPPO may improve the volatility, thermal stability, carrier-transport to electroluminescence devices and also increases the

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emission quantum efficiency (η) by protecting the metal ion from the luminescence quencher such as O–H and N–H oscillators [5].

The spectroscopic properties of the 2-acyl-1,3-indandione complexes have been only moderately studied. Up to now, the main investigation about rare earth complexes with 2-acyl-1,3-indandiones have been concerned with complexation investigation and luminescence properties of these systems in solution [6–9]. They made a correlation between the intensity parameter η for the Eu^{3+} -complexes, which was defined as the ratio between the intensity of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transitions, and dielectric constant of the solvents and the average polarizability of the ligand molecules. However, to the best of our knowledge, so far, no detailed studies of luminescence, including intensity parameters and ligand-to-metal energy transfer processes in solid state and X-rays structural information on these kinds of complexes have been reported yet.

The present work is devoted to the synthesis, characterization and study of the photoluminescence behavior of seven trivalent Eu^{3+} -complexes [$\text{Eu}(\text{ACIND})_3(\text{H}_2\text{O})_2$] and [$\text{Eu}(\text{ACIND})_3(\text{TPPO})_2$] (where ACIND is stands for the ligands 2-acetyl-1,3-indandionate (AIND), 2-isovaleryl-1,3-indandionate (ISOVIND) or 2-benzyl-1,3-indandionate (BIND) in solid state with 2-acyl-1,3-indandionates (Fig. 1). X-ray crystal structure of the [$\text{Eu}(\text{ISOVIND})_3 \cdot (\text{H}_2\text{O})$ -(EtOH)] complex is also presented, which, to our knowledge, it is the first report on structural analysis of a complex with the 2-acyl-1,3-indandione ligand. An analysis of the intramolecular energy transfer processes for these compounds was also performed by theoretical methods.

2. Experimental

2.1. Materials and methods

Carbon and hydrogen contents were determined by usual microanalytical procedures using an elemental analyzer model CHN 2400 (Perkin–Elmer). Infrared spectra were recorded in the range from 4000 to 400 cm^{-1} in KBr pellets by using a Bomem model MB102 FTIR spectrophotometer. TG analysis were performed with a TG-50 thermobalance (Shimadzu) by using platinum crucibles with 2 mg of sample, under a dynamic nitrogen

atmosphere (50 mL min^{-1}) and a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. Excitation and emission spectra at room ($\sim 298 \text{ K}$) and liquid nitrogen temperatures were collected at an angle of 22.5° (front face) in a spectrofluorimeter (SPEX-Fluorolog 2) with double grating 0.22 m monochromator (SPEX 1680), and a 450 W Xenon lamp as excitation source. Luminescence decay curves were measured using a phosphorimeter SPEX 1934D accessory coupled to the spectrofluorimeter.

All reagents diethyl phthalate, acetone, methyl isobutyl ketone, acetophenone and Eu_2O_3 were purchased from Aldrich Chemical Co., $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ were prepared according to Ref. [10] by reaction between europium oxide and hydrochloric acid.

2.2. Synthesis of the ligands

2-Acetyl-1,3-indandione (AIND), 2-isovaleryl-1,3-indandione (ISOVIND) and 2-benzoyl-1,3-indandione (BIND) ligands were synthesized using a method reported by Kilgore and co-workers [11]. Firstly, sodium ethoxide was formed by reacting 5.7 g (0.25 mol) of sodium with 12 mL (0.25 mol) of dried ethanol in benzene (200 mL), under stirring. A mixture of 55.5 g (0.25 mmol) of diethyl phthalate and the appropriate methyl ketone (acetone, isopropyl methyl ketone or acetophenone) was added, and refluxed at $80 \text{ }^\circ\text{C}$ for 6 h. After that, the solvent was evaporated under reduced pressure to give a yellow precipitate, which was diluted in 1 L of water and it was allowed to stand overnight. After acidifying with hydrochloric acid a yellow oil was produced, which after 24 h yield a solid product. This product was filtered, dried and recrystallized in methanol to give compound in 40% yield.

Anal. Calc. for AIND, $\text{C}_{11}\text{H}_8\text{O}_3$: C, 70.20; H, 4.30. Found: C, 69.48; H, 4.35%. IR (KBr, cm^{-1}): 3416br, 1762w, 1712s, 1660s, 1627s, 1593s, 1424s, 1390s, 1367s, 1209s, 1147m, 876s, 740s, 695m, 543m. For ISOVIND, $\text{C}_{14}\text{H}_{14}\text{O}_3$: C, 73.02; H, 6.13. Found: C, 72.48; H, 5.67%. IR (KBr, cm^{-1}): 3440br, 2962m, 1713s, 1651s, 1584s, 1465w, 1398w, 1330m, 1286w, 1218m, 1139m, 886s, 745s, 650w. For BIND, $\text{C}_{16}\text{H}_{10}\text{O}_3$: C, 76.80; H, 4.03. Found: C, 77.04; H, 4.16%. IR (KBr, cm^{-1}): 3439br, 3055w, 1711s, 1649s, 1599s, 1559s, 1497m, 1441m, 1401m, 1333s, 1293m, 1169m, 927m, 740s, 684m, 622m, 531w.

2.3. Synthesis of the hydrated Eu^{3+} -complexes

The preparation method of europium indandionate complexes were similar to those used in Ref. [12]. Sodium 2-acetyl-1,3-indandionate was prepared by neutralizing 1.0 g (5.3 mmol) of the ligand 2-acetyl-1,3-indandione with NaOH (1 mol L^{-1}) using deionized water and pH adjusted to 7. To the resulting solution was added dropwise an aqueous solution of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (0.5 g, 1.4 mmol), forming immediately a yellow precipitated that was filtered, washed with water and dried under vacuum to give the desired product (yields $\sim 90\%$). The same procedure, was

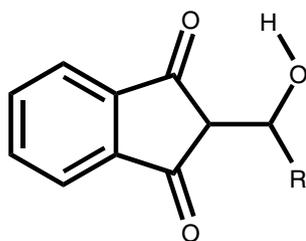


Fig. 1. Structural formula of the 2-acyl-1,3-indandione ligands.

used to synthesize hydrated Eu^{3+} -complex with 2-isovaleryl-1,3-indandionate and 2-benzoyl-1,3-indandionate ligands. In the case of the hydrated Eu^{3+} -complex with ISOVIND, a single crystal suitable for X-ray structure analysis was obtained by slow evaporation from an ethanol solution. The compositions of the complexes were confirmed by elemental analysis:

Anal. Calc. for $[\text{Eu}(\text{AIND})_3(\text{H}_2\text{O})_2]$, $\text{C}_{33}\text{H}_{25}\text{EuO}_{11}$: C, 52.88; H, 3.36. Found: C, 52.58; H, 3.83%. IR (KBr, cm^{-1}): 3452m, 1676s, 1624s, 1582s, 1510s, 1565s, 1357s, 1211m, 1155m, 1082w, 987m, 885m, 736s, 662m, 534s. For $[\text{Eu}(\text{ISOVIND})_3(\text{H}_2\text{O})_2]$, $\text{C}_{42}\text{H}_{43}\text{EuO}_{11}$: C, 57.60; H, 4.95. Found: C, 58.30; H, 4.69%. IR (KBr, cm^{-1}): 3415m, 3068m, 2956m, 2870m, 1680s, 1620s, 1579s, 1465s, 1355s, 1284m, 1207m, 1155m, 1072m, 894m, 734s, 667m, 670w, 530m. For $[\text{Eu}(\text{ISOVIND})_3(\text{H}_2\text{O})(\text{EtOH})]$, $\text{C}_{44}\text{H}_{47}\text{EuO}_{11}$: C, 58.47; H, 5.24. Found: C, 58.33; H, 5.20%. IR (KBr, cm^{-1}): 3367m, 3078m, 2952m, 2867m, 1677s, 1629s, 1585s, 1510s, 1470s, 1650s, 1282m, 1205m, 1153m, 1072m, 896m, 733m, 654m, 532m. For $[\text{Eu}(\text{BIND})_3(\text{H}_2\text{O})_2]$. Calc. for $\text{C}_{48}\text{H}_{31}\text{EuO}_{11}$: C, 61.61; H, 3.34. Found: C, 61.68; H, 3.27%. IR (KBr, cm^{-1}): 3427m, 3062m, 1620s, 1585s, 1490s, 1454s, 1425s, 1363m, 1153w, 885m, 800w, 742m, 702m, 640m, 534m.

2.4. Synthesis of the Eu^{3+} -complexes with TPPO

Europium complexes with TPPO as a second kind of ligand were synthesized using the correspondent hydrated $[\text{Eu}(\text{ACIND})_3(\text{H}_2\text{O})_2]$ complexes as precursors. A solution of TPPO (0.37 g, 1.3 mmol) in acetone (10 mL) was added to a solution of $[\text{Eu}(\text{ACIND})_3(\text{H}_2\text{O})_2]$ (0.5 g, ~ 0.6 mmol) in acetone (20 mL), and the mixture was stirred for 2 h at room temperature. After solvent evaporation, a precipitated was produced, which was filtered, washed with ethanol and dried in vacuum. Yield: $\sim 80\%$. The compositions of the complex systems were confirmed by elemental analysis and IR data: *Anal. Calc.* for $[\text{Eu}(\text{AIND})_3(\text{TPPO})_2]$, $\text{C}_{69}\text{H}_{51}\text{EuO}_{11}\text{P}_2$: C, 65.25; H, 4.05. Found: C, 64.93; H, 4.11%. IR (KBr, cm^{-1}): 3107m, 1558s, 1531s, 14317s, 1396s, 1342m, 1227m, 1120m, 1080w, 1037m, 862m, 820s, 777s, 725s, 659m, 430m. For $[\text{Eu}(\text{ISOVIND})_3(\text{TPPO})_2]$, $\text{C}_{78}\text{H}_{69}\text{EuO}_{11}\text{P}_2$: C, 67.09; H, 4.98. Found: C, 67.04; H, 5.27%. IR (KBr, cm^{-1}): 3056m, 1689m, 1589s, 1491m, 1452s, 1425s, 1362m, 1340m, 1340m, 1167m, 1118m, 1018w, 881m, 798w, 742m, 694m, 636m, 540s. For $[\text{Eu}(\text{BIND})_3(\text{TPPO})_2]$, $\text{C}_{84}\text{H}_{57}\text{EuO}_{11}\text{P}_2$: C, 69.28; H, 3.95. Found: C, 69.06; H, 3.83%. IR (KBr, cm^{-1}): 3055w, 1687m, 1620s, 1589s, 1490m, 1452s, 1425s, 1340m, 1164m, 1121m, 1020w, 743m, 696m, 636m, 540s.

2.5. X-ray structure determination of $\text{Eu}(\text{ISOVIND})_3(\text{H}_2\text{O})(\text{EtOH})$

A suitable crystal of the $\text{Eu}(\text{ISOVIND})_3(\text{H}_2\text{O})(\text{EtOH})$ complex for X-ray diffraction was obtained dissolving the complex in a mixture of ethanol and water in a ratio

3/1 (v/v). The resulting solution was kept in stand by for a week, resulting in yellow hexagonal crystals. A crystal of this compound was mounted in a Enraf-Nonius CAD4 diffractometer with graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$), at 293 K. The structure was solved by direct methods using the SIR92 program [13] and refined by full-matrix least-squares methods on F^2 by the SHELX97 program package [14]. The hydrogen atoms for the water molecule was found in the Fourier difference map, and refined with U equal to 1.3 times the U_{eq} of the Ow. All others non-hydrogen atoms were refined anisotropically and the hydrogen atoms position were calculated in ideal geometry with thermal parameters equal to 1.5 times the U_{eq} of the attached C atom for the methyl groups and 1.2 for the others. Crystallographic data for the $\text{Eu}(\text{ISOVIND})_3(\text{H}_2\text{O})(\text{EtOH})$ complex are shown in Table 1.

3. Results and discussion

IR spectra of the complexes as compared to the free indandione ligands show a displacement of the $\text{C}=\text{O}$ stretching to lower frequencies (about 70 cm^{-1}), suggesting that the indandionate ligands are coordinated through oxygen atoms. In the case of the complexes $\text{Eu}(\text{ACIND})_3(\text{TPPO})_2$, the displacement of the $\text{P}=\text{O}$ stretching from 1190 cm^{-1} in the free TPPO ligand to 1170 cm^{-1} in the compounds provides good evidence that the coordination of the TPPO to europium ion is also occurring through oxygen atom.

Table 1
Crystal data and structure refinement for the $[\text{Eu}(\text{ISOVIND})_3(\text{H}_2\text{O})(\text{EtOH})]$ complex

Formula	$\text{C}_{44}\text{H}_{47}\text{EuO}_{11}$
Formula weight	903.78
Crystal system	monoclinic
Space group	$P2_1/n$ (no. 14)
a (\AA)	15.361(1)
b (\AA)	18.364(2)
c (\AA)	15.705(2)
β ($^\circ$)	106.373(8)
V (\AA^3)	4250.6(8)
Z	4
D_{calc} (g/cm^3)	1.412
μ ($\text{Mo K}\alpha$) (mm^{-1})	1.533
$F(000)$	1848
Crystal size (mm)	$0.08 \times 0.10 \times 0.15$
Temperature (K)	293
Radiation (\AA) $\text{Mo K}\alpha$	0.71069
θ (Min.–Max.) ($^\circ$)	2.6, 28.5
Data set hkl , min:max	–19:20; 0:24; –21:0
Total, unique data, R_{int}	11 178, 10809, 0.054
Observed data [$I > 2\sigma(I)$]	4859
N_{ref} , N_{par}	10809, 518
R , wR_2 , S	0.0516, 0.1360, 0.94
Maximum and average shift/error	0.22, 0.01
Minimum and maximum residual density [e/\AA^3]	–0.89, 0.78

$$w = 1/\sigma^2(F_o^2) + 0.0517P^2 \text{ where } P = (F_o^2 + 2F_c^2)/3.$$

Thermogravimetric curves for the $[\text{Eu}(\text{ACIND})_3(\text{H}_2\text{O})_2]$ complexes exhibited similar profiles (figure not shown). The curves show a first weight loss in the range from 120 to 190 °C, which is assigned to the release of two water molecules coordinated to the Eu(III) ion. For $[\text{Eu}(\text{ISOVIND})_3(\text{H}_2\text{O})(\text{EtOH})]$ complex the first weight loss corresponds to 6.8%, which agrees to the release of one water and one ethanol molecule. The complexes with the TPPO ligand present no weight loss until 230 °C, confirming the anhydrous character of these complexes.

3.1. Structure of $[\text{Eu}(\text{ISOVIND})_3(\text{H}_2\text{O})(\text{EtOH})]$

X-ray analysis reveals that eight oxygen atoms are coordinated to the central europium ion (six from the bidentate ISOVIND ligand, one from the water molecule and another from the ethanol). A key feature of the structure described herein is that, to the best of our knowledge, it is the first example of a rare earth coordination compound with a 2-acyl-1,3-indandionate ligand to be reported. The carbon atoms $-\text{CH}_2$ and $-\text{CH}_3$ from the ligands (2-acyl-1,

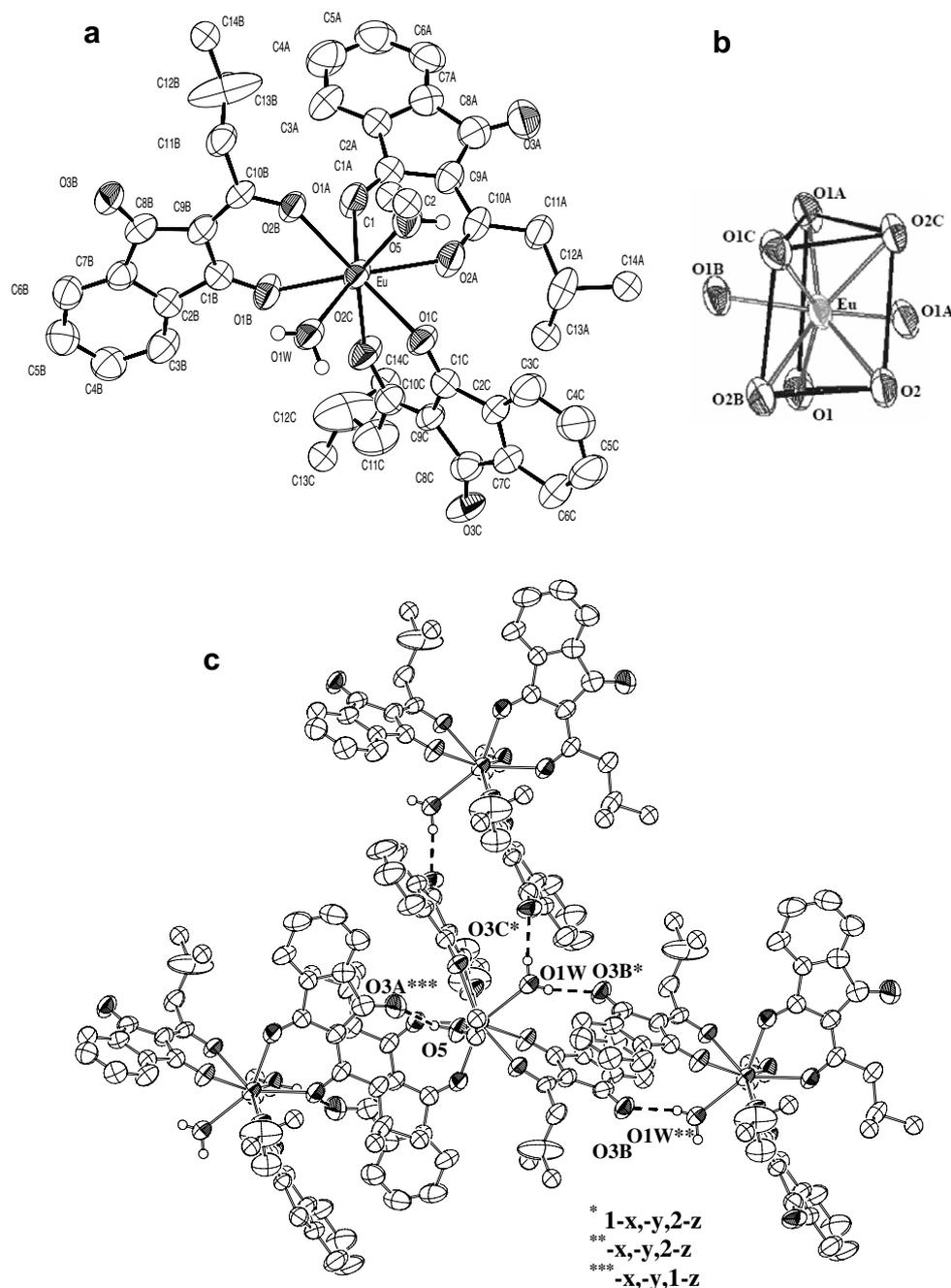


Fig. 2. (a) ORTEP drawing (50% of probability) displaying the X-ray structure of $[\text{Eu}(\text{ISOVIND})_3(\text{H}_2\text{O})(\text{EtOH})]$ complex; the thermal disordered methyl carbon atoms are arbitrary taken with Ueq equal to 0.05. (b) Coordination polyhedron of Eu^{3+} ion and (c) Molecules of $[\text{Eu}(\text{ISOVIND})_3(\text{H}_2\text{O})(\text{EtOH})]$ complex showing intermolecular H-bonding connections as dashed lines.

3-indandionate and ethanol) presents disorder by the thermal vibration. An ORTEP drawing displaying the molecular structure, with the methyl carbon atoms assuming an isotropical displacement supposition, the coordination polyhedron of the Eu(III) ion, and representation of the intermolecular hydrogen bonds in $[\text{Eu}(\text{ISOVIND})_3(\text{H}_2\text{O})(\text{EtOH})]$, are presented in Fig. 2.

The geometrical arrangement of the oxygen atoms in the first coordination sphere can be described as a bicapped trigonal prism presenting a site symmetry close to C_{2v} (Fig. 2b). The Eu–O distances fall into two distinct ranges where those including O atoms from ISOVIND are shorter (Eu–O \sim 2.40 Å) than those from neutral aqua and ethanol ligands, which present Eu–O distances of 2.422(5) and 2.447(4) Å, respectively (Table 2). It is also important to observe in the crystal structure of $\text{Eu}(\text{ISOVIND})_3(\text{H}_2\text{O})(\text{EtOH})$ that the hydrogen bond scheme (Table 2) gives rise to a supermolecular polymer (Fig. 2c). The water molecule coordinated to the Eu^{3+} ion is simultaneously hydrogen-bonded to two uncoordinated carbonyl oxygen atom of ISOVIND of two adjacent molecules (symmetry operation $\bar{1}$), and the OH from ethanol is connected to the third CO group of ISOVIND through O–H...O hydrogen bonds. The $\text{O}_{\text{water}}\text{--H}\cdots\text{O}_{\text{carbonyl}}$ hydrogen bonds are similar to those found for rare earth complexes with aliphatic β -diketonate ligands reported in the literature [15].

Excitation spectra of the europium complexes with 2-acyl-1,3-indandione ligands, recorded at 77 K in the spectral range 250–590 nm (Fig. 3) were obtained with emission monitored at ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ hypersensitive transition around

Table 2
Selected bond distances (Å), angles ($^\circ$) and hydrogen bonds in the $[\text{Eu}(\text{ISOVIND})_3(\text{H}_2\text{O})(\text{EtOH})]$ complex

Distance (Å)							
Eu–O1a	2.400(4)	Eu–O2a	2.401(5)				
Eu–O1b	2.403(4)	Eu–O2b	2.382(3)				
Eu–O1c	2.410(5)	Eu–O2c	2.348(4)				
Eu–O1w	2.420(5)	Eu–O5	2.448(4)				
Angles ($^\circ$)							
O1a–Eu–O1b	78.5(2)	O1c–Eu–O2a	69.8(2)				
O1a–Eu–O1c	140.9(2)	O1c–Eu–O2b	132.7 (1)				
O1a–Eu–O1w	149.5(2)	O1c–Eu–O2c	73.0(1)				
O1a–Eu–O2a	71.2(2)	O1c–Eu–O5	74.0(2)				
O1a–Eu–O2b	76.2(2)	O1w–Eu–O2a	139.3(2)				
O1a–Eu–O2c	98.2(1)	O1w–Eu–O2b	80.1(2)				
O1a–Eu–O5	97.2(1)	O1w–Eu–O2c	89.6(2)				
O1b–Eu–O1c	129.9(2)	O1w–Eu–O5	93.8(2)				
O1b–Eu–O1w	76.3(2)	O2a–Eu–O2b	129.2(2)				
O1b–Eu–O2a	134.0(1)	O2a–Eu–O2c	79.8(2)				
O1b–Eu–O2b	72.5(2)	O2a–Eu–O5	74.0(1)				
O1b–Eu–O2c	71.17(2)	O2b–Eu–O2c	143.6(2)				
O1b–Eu–O5	145.0(2)	O2b–Eu–O5	72.7(2)				
O1c–Eu–O1w	69.6(2)	O2c–Eu–O5	143.3(2)				
A	H	B	<i>d</i> (A–H) (Å)	<i>d</i> (H...B) (Å)	<i>d</i> (A...B) (Å)	Angle ($^\circ$)	Symmetry operation
Hydrogen bonds for the $[\text{Eu}(\text{ISOVIND})_3(\text{H}_2\text{O})(\text{EtOH})]$ complex							
O1w	H1Ow	O3b	0.76(8)	1.98(8)	2.717(7)	166(8)	1 – x, –y, 2 – z
O1w	H2Ow	O3c	0.87(8)	1.93(8)	2.793(7)	168(5)	–x, –y, 2 – z
O5	H1O5	O3a	0.93	2.12	2.770(7)	125	–x, –y, 1 – z

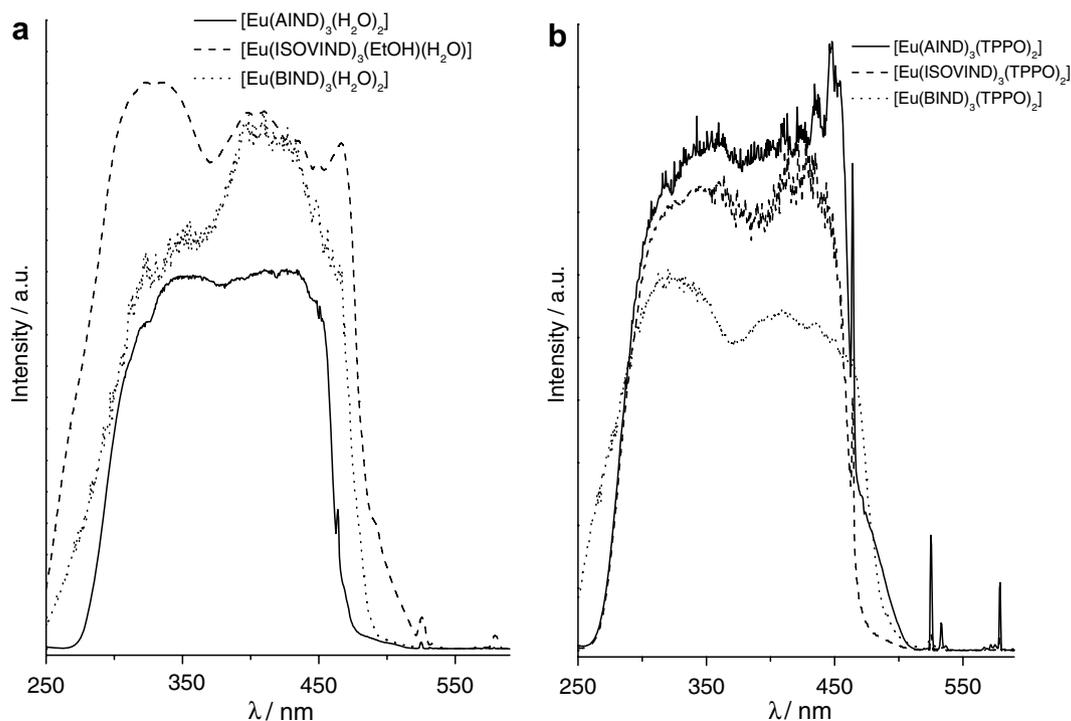


Fig. 3. Excitation spectra of (a) $[\text{Eu}(\text{ACIND})_3 \cdot (\text{H}_2\text{O})_2]$ and (b) $[\text{Eu}(\text{ACIND})_3 \cdot (\text{TPPO})_2]$ complexes in solid state, at 77 K. The spectra were recorded with emission monitored at 612 nm.

612 nm. These spectra present a strong broad band between 270 and 470 nm assigned to the photoexcitation process of the Eu(III) ion via the $S_0 \rightarrow S_1$ transition. The excitation spectra also exhibit narrow bands assigned to the 4f–4f transitions from the 7F_0 ground level to the excited states. However, these bands are less intense than those bands corresponding to the $S_0 \rightarrow S_1$ transition. This result gives evidence of europium luminescence sensitization through intramolecular energy transfer from the 2-acyl-1,3-indandione ligands.

Photoluminescence spectra of the hydrated complexes and those with the TPPO ligand, at 77 K, are displayed in Fig. 4. The emission spectra show characteristic ${}^5D_0 \rightarrow {}^7F_J$ ($J = 0-4$) transitions of Eu(III), with the hypersensitive ${}^5D_0 \rightarrow {}^7F_2$ transition (at 612 nm) as the most prominent one. The local-ligand field splitting is particularly evident for ${}^5D_0 \rightarrow {}^7F_{1-4}$ transitions, presenting Stark ($2J + 1$)-components, indicating that the Eu^{3+} ion occupies a site with low symmetry [16,17]. It is observed that, in general, emission spectra of complexes with TPPO present different profiles from the respective hydrated compounds, reflecting changes in the chemical environment around the Eu^{3+} ion. It is also important to mention that the emis-

sion spectra of all europium complexes do not exhibit ligand centered transitions, indicating that there is an efficient intramolecular energy transfer from the indandionate ligands to the Eu^{3+} ion.

In order to get further information on the chemical environment of the Eu^{3+} ions in these complexes, experimental intensity parameters Ω_2 ($\lambda = 2$ and 4), radiative rates (A_{0J}) for the ${}^5D_0 \rightarrow {}^7F_2$ and ${}^5D_0 \rightarrow {}^7F_4$ transitions and emission quantum efficiency (η) were determined (Table 3) according to Refs. [16,18].

Experimental intensity parameter Ω_2 exhibits values around $40 \times 10^{-20} \text{ cm}^2$ for the hydrated complexes, suggesting the presence of a highly polarizable chemical environment around the Eu^{3+} ion [5]. These values are as high as those presented for europium complexes containing aliphatic β -diketonate, such as TTA and DBM-europium complexes [3]. It is also observed a decrease in Ω_2 for complexes with TPPO as compared to the hydrated ones. This result may be a consequence of steric hindrance due to phenyl groups that belong to the TPPO ligand.

Comparing the values of η for the complexes containing the TPPO ligand with their respective hydrated compounds, it is concluded that indeed a substitution of water

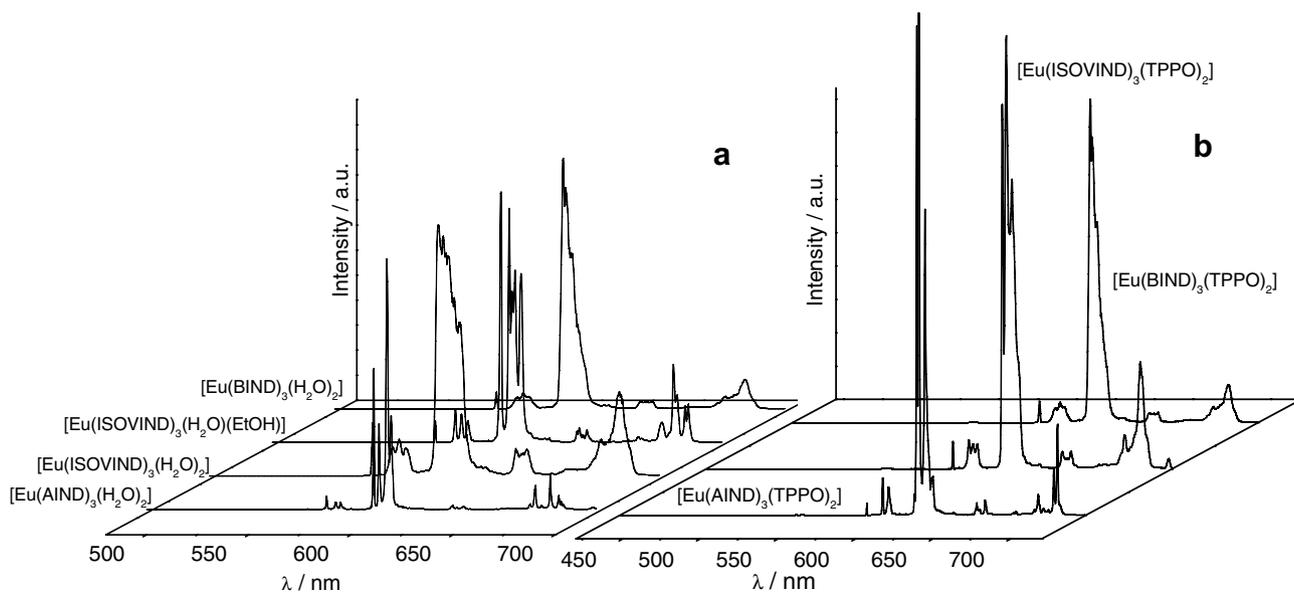


Fig. 4. Emission spectra of (a) $[\text{Eu}(\text{ACIND})_3 \cdot (\text{H}_2\text{O})_2]$ and (b) $[\text{Eu}(\text{ACIND})_3 \cdot (\text{TPPO})_2]$ complexes in solid state, at 77 K, recorded under excitation at 350 nm.

Table 3

Intensity parameters (Ω_2), radiative (A_{rad}), non-radiative (A_{nrad}) rates and emission quantum efficiency of the 5D_0 emitting level determined for the 2-acyl-1,3-indandionate complexes

Compound	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	τ (ms)	A_{rad} (s^{-1})	A_{nrad} (s^{-1})	A_{tot} (s^{-1})	η (%)
$[\text{Eu}(\text{AIND})_3 \cdot (\text{H}_2\text{O})_2]$	42.1	14.8	0.1079	1532	7739	9261	16.5
$[\text{Eu}(\text{AIND})_3 \cdot (\text{TPPO})_2]$	35.5	8.9	0.5309	1255	628	1883	66.7
$[\text{Eu}(\text{ISOVIND})_3 \cdot (\text{H}_2\text{O})_2]$	40.4	15.8	0.0387	1499	24330	25830	5.8
$[\text{Eu}(\text{ISOVIND})_3 \cdot (\text{H}_2\text{O})(\text{EtOH})]$	40.9	17.5	0.056	1537	16320	17860	8.6
$[\text{Eu}(\text{ISOVIND})_3 \cdot (\text{TPPO})_2]$	35.3	11.4	0.5071	1283	688	1972	65.1
$[\text{Eu}(\text{BIND})_3 \cdot (\text{H}_2\text{O})_2]$	40.5	14.2	0.0539	1482	17080	18560	8.0
$[\text{Eu}(\text{BIND})_3 \cdot (\text{TPPO})_2]$	29.4	15.9	0.3181	1165	1978	3143	37.1

molecules in the first coordination sphere of the Eu^{3+} ion by the TPPO ligand occurs. This result reflects a decrease in the non-radiative rates (A_{nrad}) that is a consequence of the absence of O–H oscillators present in coordinated water molecules, which causes multiphonon deactivation process in the Eu^{3+} ion [5].

Theoretical structure for the $[\text{Eu}(\text{ISOVIND})_3(\text{H}_2\text{O})(\text{EtOH})]$ complex was calculated using the Sparkle/AM1 model [16]. The result obtained agrees with those determined by X-rays diffraction (Fig. 2), indicating that the Sparkle/AM1 model has also proved to be very useful in predicting coordination geometries of the Eu-indandionate complexes.

Theoretical quantum yield, q , for $[\text{Eu}(\text{ISOVIND})_3(\text{H}_2\text{O})(\text{EtOH})]$ was calculated according to the procedure described in Refs. [4,19]. The calculated values of transfer (W_{ET}) and back-transfer (W_{BT}) rates between ligand and Eu^{3+} ion levels are the following: $\text{S}_1 \rightarrow {}^5\text{D}_2$, $W_{\text{ET}} = 4.42 \times 10^6 \text{ s}^{-1}$; $\text{S}_1 \rightarrow {}^5\text{D}_1$, $W_{\text{ET}} = 1.30 \times 10^{10} \text{ s}^{-1}$; $\text{S}_1 \rightarrow {}^5\text{D}_0$, $W_{\text{ET}} = 9.5 \times 10^9 \text{ s}^{-1}$; $\text{T} \rightarrow {}^5\text{D}_1$, $W_{\text{ET}} = 5.45 \times 10^9 \text{ s}^{-1}$ ($W_{\text{BT}} = 4.95 \times 10^9 \text{ s}^{-1}$); $\text{T} \rightarrow {}^5\text{D}_0$, $W_{\text{ET}} = 6.16 \times 10^9 \text{ s}^{-1}$ ($W_{\text{BT}} = 1.37 \times 10^6 \text{ s}^{-1}$). The back-transfer (W_{BT}) rates ${}^5\text{D}_J \rightarrow \text{S}_1$ are negligible. Consequently, there are two probable intramolecular energy transfer processes as operative channels from ISOVIND to the Eu^{3+} ion in $[\text{Eu}(\text{ISOVIND})_3(\text{H}_2\text{O})(\text{EtOH})]$: (1) $\text{S}_0 \rightarrow \text{S}_1 \rightarrow \text{T} \rightarrow ({}^5\text{D}_1, {}^5\text{D}_0) \rightarrow {}^7\text{F}_J$ and (2) $\text{S}_0 \rightarrow \text{S}_1 \rightarrow ({}^5\text{D}_1, {}^5\text{D}_0) \rightarrow {}^7\text{F}_J$. Besides, the value of q (8.0%) is close to $\eta = 8.6\%$, indicating that an efficient energy transfer from indandionate ligands to the Eu^{3+} ion in fact occurs.

4. Conclusions

It has been demonstrated that the first structurally characterized Eu^{3+} –(2-acyl-1,3-indandione) complex indicated that their coordination to the metal ion occurs in similar form as for aliphatic β -diketonates. Our results indicate that an efficient ligand-metal ion energy transfer process occurs for the Eu–(2-acyl-1,3-indandione) complexes, and that the channels (1) and (2) are the most probable ones involved in photoluminescent mechanism for $[\text{Eu}(\text{ISOVIND})_3(\text{H}_2\text{O})(\text{EtOH})]$ complex.

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Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structure have been with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 296851. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code + 44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk]. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.06.035.

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