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1-Methyl-1,10-phenanthrolin-2(1*H*)-one (**L**) as a ligand to Eu(III): Crystal structure and luminescent properties of $[Eu(\mathbf{L})_3(NO_3)_3]$

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ABSTRACT

A new coordination compound of Eu(III) with 1-methyl-1,10-phenanthroline-2(1*H*)-one (**L**) as a ligand has been synthesized and characterized using infrared spectroscopy, elemental analysis and single crystal X-ray diffraction. The structure contains isolated $[Eu(\mathbf{L})_3(NO_3)_3]$ molecules interacting through extensive π-stacking. Photoluminescence studies demonstrate that the complex shows line-like emission characteristic of Eu(III) when excited in the ligand-centered absorption bands, with a quantum yield of 22% and a lifetime of 0.74 ms.

1. Introduction

Ever since the discovery of the antenna effect in 1942, complexes with trivalent lanthanoid ions have been widely studied for their luminescent properties. The trivalent lanthanoid ions show interesting photophysical properties, such as narrow line-like emission and lifetimes in the millisecond range, as a result of the intraconfigurational 4f–4f transitions [1,2]. Strictly, these transitions are forbidden by the Laporte selection rule and in addition many of them are spin forbidden. As a result, the absorption by 4f–4f transitions cannot be used to efficiently excite the trivalent lanthanoid ions. It was found by Weissman that suitable organic ligands can act as an antenna that absorbs light *via* allowed transitions and subsequently transfers the acquired energy to the lanthanoid ion [3]. This mechanism, also known as sensitization, can greatly enhance the luminescence intensity of the lanthanoid ions, allowing application in for example sensors [1,4] and bio-assays [5]. The luminescence of Eu(III) is of particular interest, as its strongest emission line is in the visible region around 614 nm. In principle, this means that Eu(III)-based complexes are attractive for application as a red-emitting phosphor material in phosphor converted white light emitting diodes (PC-WLEDs). In PC-WLEDs, the emission of a near UV or blue-emitting LED is converted into white light by suitable phosphor materials, thereby turning the intrinsically monochromatic emission of an LED into white light [6,7]. Currently, phosphors that exhibit efficient line-like emission in the red region with good absorption properties in the near UV to blue spectral region (370–470 nm) are still lacking, necessitating research in this area [6].

Ligands that are known to efficiently sensitize Eu(III) luminescence are beta-diketones [8–10], aromatic carboxylates [11–13], and calixarenes [14]. 1,10-Phenanthrolines form another class of widely used antenna ligands, and the resulting Eu(III) complexes exhibit bright photoluminescence upon excitation in ligand centered absorption bands [15–17]. During our investigation of the influence of substituents on 1,10-phenanthroline on the photoluminescent properties of the Eu(III) complexes, out of curiosity one of the synthetic intermediates, 1-methyl-1,10-phenanthrolin-2(1*H*)-one (**L**) shown in Fig. 1, was used as a ligand for Eu(III) [18]. We were surprised by the relatively easy formation of a complex with a poor ketone-type ligand. To the best of our knowledge, this molecule has never been used before as a ligand. In this paper, we report the synthesis, crystal structure and photoluminescent properties of the resulting complex which is described by the formula $[Eu(L)_3(NO_3)_3]$.

2. Experimental

2.1. General

NMR spectra were recorded on a Bruker DPX300. IR spectra were measured with a Perkin Elmer Paragon 1000 FTIR equipped

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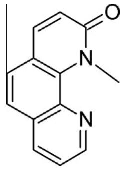

Fig. 1. Schematic drawing of 1-methyl-1,10-phenanthrolin-2(1*H*)-one (**L**).

with a Golden Gate ATR. Luminescence data were collected using a Shimadzu RF-5300PC spectrofluorophotometer equipped with a solid-state sample holder. For determination of photoluminescence quantum yields, an Edinburgh Instruments FLS920 spectrophotometer equipped with an integrating sphere was used. For determination of luminescence lifetime, this spectrometer was used together with a pulsed laser excitation source. Phenanthroline was purchased from Merck and used as received.

*2.2. Synthesis of 1-methyl-1,10-phenanthrolin-2(1H)-one (**L**)*

The ligand was prepared following literature procedures. Phenanthroline was oxidized to its N-oxide using dihydrogen peroxide following the methods reported by Engbersen and Corey [19,20]. Subsequently, the N-oxide was converted to 1-methyl-1,10-phenanthrolin-2(1*H*)-one using dimethyl sulfate, following the procedure reported by Kolling [21]. Overall yield: 86%. ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 8.94 (dd, 1H), 8.18 (dd, 1H), 7.79 (d, 1H), 7.56 (m, 2H), 7.50 (dd, 1H), 6.91 (d, 1H), 4.49 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 147.3, 139.2, 136.2, 126.8, 122.5, 122.3, 122.0, 38.0. IR ν/cm^{-1}:1657(vs), 1646(vs), 1602(vs), 1539(s), 1505(s), 1468(s), 1418(m), 1271(m), 1196(m), 1166(w), 1128(s), 1035(m), 989(m), 911(m), 843(vs), 783(s), 732(s), 705(s), 656(s), 604(s), 577(m), 546(m), 463(vs).

2.3. Synthesis of $[Eu(\mathbf{L})_3(NO_3)_3]$

0.25 g (1.2 mmol) of **L** was dissolved in 15 mL of ethanol and heated to boiling for 15 min until complete dissolution of **L**. To this solution was slowly added a boiling solution of 0.17 g (0.4 mmol) $Eu(NO_3)_3{\cdot}5H_2O$ in 10 mL ethanol. The mixture was boiled and stirred for 15 more minutes and cooled down to room temperature, and the resulting precipitate was collected by filtration, washed with ethanol and allowed to dry in air. Yield 200 mg, 50% based on Eu, of a light yellow powder. IR ν/cm^{-1}: 1640(s), 1616(w), 1600(m), 1564(s), 1558(s), 1538(vs), 1496(s), 1472(vs), 1456(vs), 1436(m), 1424(s), 1404(s), 1291(br, vs), 1236(s), 1200(m), 1168(m), 1144(m), 1026(s), 989(m), 922(m), 848(vs), 831(m), 816(m), 780(s), 736(s), 708(vs), 668(m), 658(s), 604(s), 578(m), 547(m), 527(m), 478(vs), 398(w), 358(m), 336(w), 326(m), 318(m). Elemental *Anal.* Calc. for $C_{39}H_{30}EuN_9O_{12}$ ($Eu(\mathbf{L})_3(NO_3)_3$): C, 48.36; H, 3.12; N, 13.01. Found: C, 48.88; H, 3.18; N, 13.26%.

2.4. Structure determination

Crystals suitable for single crystal X-ray diffraction were grown by slow diffusion of an ethanolic solution of 0.10 g (0.48 mmol) of ligand into an ethanolic solution of 0.067 g (0.16 mmol) of $Eu(NO_3)_3{\cdot}5H_2O$ in a Y-tube over a period of 3 weeks. Crystals appeared as large orange blocks of sizes up to 0.5 × 0.5 × 2.0 mm^3.

Crystallographic data and refinement details are given in Table 1. A crystal was selected for the X-ray measurements and mounted to the glass fiber using the oil drop method [22] and data were collected at 173 K on a Nonius Kappa CCD diffractometer (Mo Kα radiation, graphite monochromator, λ = 0.71073). The intensity data were corrected for Lorentz and polarization effects, and for absorption. The programs COLLECT [23], SHELXS-97 [24], SHELXL-97 [24,25] were used for data reduction, structure solution and structure refinement, respectively. The non-hydrogen atoms were refined anisotropically. The H atoms were introduced in calculated positions and refined isotropically riding with fixed geometry with respect to their carrier atoms.

Table 1
Crystallographic details for $[Eu(L)_3(NO_3)_3]$.

Formula	$C_{39}H_{30}EuN_9O_{12}$
FW	968.68
Crystal size (mm)	0.20 × 0.20 × 0.10
Crystal color	orange
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	10.296(1)
b (Å)	12.478(1)
c (Å)	15.661(2)
α (°)	77.45(1)
β (°)	85.95(1)
γ (°)	69.52(1)
V (Å^3)	1839.8(4)
Z	2
d_{calc} (g/cm^3)	1.749
μ (mm^{-1})	1.786
Reflections measured/unique	29148/8357
Parameters	553
R_1 ($I > 2\sigma(I)$)/wR_2 (all reflections)	0.026/0.056
S	1.09
$\rho_{min/max}$ (e/Å^3)	−0.50/0.69

3. Results and discussion

3.1. Synthesis and characterization

The ligand was obtained in a satisfactory yield following the literature procedures [19–21]. The ^{1}H NMR spectrum of the ligand clearly shows the presence of the *N*-methyl group as a singlet at 4.49 ppm and the presence of only seven aromatic protons. The presence of the carbonyl group is revealed in the IR by the strong band around 1650 cm^{-1}, indicating that the ligand has formed. The complex synthesis was performed in boiling ethanol; extended boiling of the ligand is necessary to ensure complete dissolution and the complex mixture was boiled to slow down precipitation of the complex. After 15 min of stirring, formation of additional precipitate was observed. Due to the large number of vibrations, full assignment of the IR spectrum is complicated. Nevertheless, Tsaryuk et al. have performed detailed analysis on the vibrational spectra of similar Eu(III) complexes with phenanthroline-type ligands [26]. Based on this work, the absorption bands at 708, 736, 816, 1026, 1291 and 1470 cm^{-1} can be assigned to vibrational modes of the nitrate ligands. Bands resulting from the phenanthrolone ligand appear at 604, 658, 781, 848, 1638, 1496 and 1543 cm^{-1} [27].

3.2. Description of the crystal structure

A projection of the crystal structure of $[Eu(\mathbf{L})_3(NO_3)_3]$ is given in Fig. 2 and the crystallographic data are summarized in Table 1. The structure contains a single Eu(III) ion in the asymmetric unit, and has two molecules in the unit cell. The first coordination sphere of the complex contains three ligands bonded to Eu(III) through the carbonyl oxygen of **L** and three bidentate nitrate ions, resulting in a coordination number of nine around the central ion. Interestingly, all ligands are lying in approximately parallel planes. As illustrated in Fig. 2, the geometry around the Eu(III) ion is best described as a highly distorted monocapped square antiprism with the top vertex and a corner of one of the squares being defined by nitrato oxygens, while the other three corners of this square

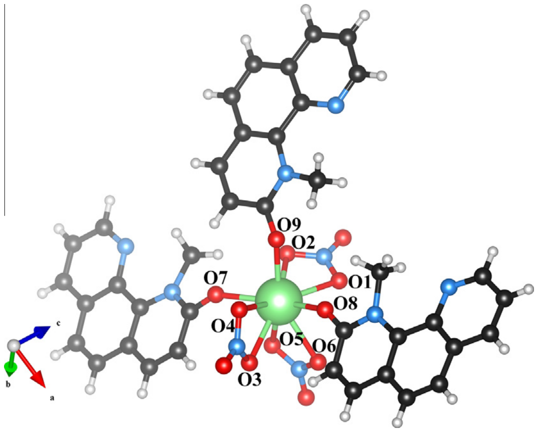

Fig. 2. Projection of the structure of $[Eu(\mathbf{L})_3(NO_3)_3]$, showing the atomic labeling scheme. The coordination sphere around Eu is approximately monocapped square antiprismatic.

are occupied by the carbonyl oxygens of the ligand. The other square face comprises four nitrato oxygen atoms. The Eu–O bond lengths are given in Table 2. They range from 2.322(1) to 2.360(2) Å for the Eu-carbonyl oxygens of the ligands, which can be considered as normal [28]. For the chelating nitrates, Eu–O bond lengths vary from 2.472(2) to 2.550(2) Å. The length of the C═O double bond varies from 1.258(3) to 1.268(4) Å, indicating a slight elongation as compared to C(sp^2)═O bonds that are around 1.20 Å on average [29]. The Eu–O–C bond angles vary markedly within the complex, as can be seen from Table 2. π-Stacking interactions play an important role in the crystal structure: the plane-to-plane distances between neighboring phenanthroline rings range from 3.227(1) to 4.097(1) Å. A number of these stacking interactions is shown in Fig. 3; the distances between the centroids in this particular stacking interaction are 3.77–4.41 Å.

3.3. Photoluminescence

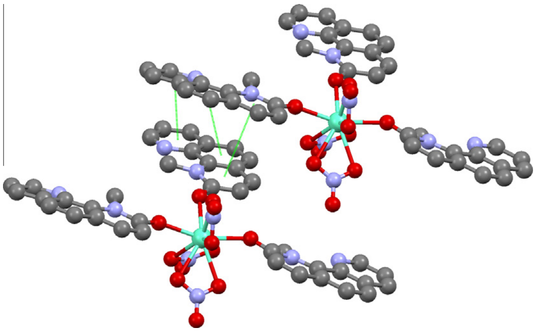

Fig. 3. Projection of $[Eu(\mathbf{L})_3(NO_3)_3]$, showing part of the π-stacking interactions.

When illuminated with a standard laboratory UV lamp emitting at 366 nm $[Eu(\mathbf{L})_3(NO_3)_3]$ shows intense red luminescence. The solid-state photoluminescence spectra of the complex recorded at room temperature are given in Fig. 4. The excitation spectrum features a broad band in the near-UV region with a maximum at 275 nm as a result of ligand-centered excitation. The small spike on the shoulder of the broad band at 395 nm can be attributed to direct excitation of the Eu(III) ion *via* the $(^5L_6, ^5G_2, ^5L_7, ^5G_3) \leftarrow {}^7F_0$ transition [30]. The emission spectrum is characteristic of Eu(III) with most of the emission intensity in the $^5D_0 \rightarrow {}^7F_2$ transition at 617 nm, indicating ligand to metal energy transfer. The intensity ratio of the hypersensitive electric dipole $^5D_0 \rightarrow {}^7F_2$ transition *versus* the magnetic dipole (MD) $^5D_0 \rightarrow {}^7F_1$ transition at 593 nm can be used as a probe for the local symmetry around Eu(III) [31]. For $[Eu(\mathbf{L})_3(NO_3)_3]$ the ratio $(^5D_0 \rightarrow {}^7F_2)/(^5D_0 \rightarrow {}^7F_1)$ is around 11. This clearly indicates the lack of an inversion centre at Eu(III), which is in agreement with the crystal structure. Furthermore, the $^5D_0 \rightarrow {}^7F_2$ transition is visibly split into two bands centered at 615 and 619 nm as a result of the crystal field around Eu(III). The intensity of the $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transitions at 651 and 691 nm is negligible. The decay profile of the intensity of the $^5D_0 \rightarrow {}^7F_2$ transition has been fitted to a single exponential function with a lifetime τ_{exp} of 0.74 ms. The radiative lifetime can be estimated from the emission profile, using the relative intensity of the emission lines with respect to the MD transition. The intensity of this transition is of a purely MD nature, and is nearly insensitive of the environment of Eu(III). Following the procedure outlined by Werts et al., and assuming a refractive index of 1.5 for $[Eu(\mathbf{L})_3(NO_3)_3]$, a value of 1.47 ms is obtained for τ_{rad} [32]. The intrinsic quantum yield can be found from τ_{exp}/τ_{rad} and equals 50%, indicating that radiative and non-radiative decay rates are similar in $[Eu(\mathbf{L})_3(NO_3)_3]$. The external photoluminescence quantum yield for $[Eu(\mathbf{L})_3(NO_3)_3]$was found to be 22%. Compared to other Eu(III)-complexes, this indicates fairly efficient photoluminescence. From this value and the intrinsic quantum efficiency, the sensitization efficiency η_{sens} can be calculated to be 44% [33]. These values indicate that non-radiative decay processes of the $^5D_0$ state compete effectively with the radiative processes, and that **L** acts as a moderately efficient antenna. The photophysical parameters of $[Eu(\mathbf{L})_3(NO_3)_3]$ are listed in Table 3. Direct comparison of these parameters to those determined for other Eu(III)-phenanthroline complexes seems inappropriate. The methyl group at

Table 2
Selected bond distances and angles for $[Eu(\mathbf{L})_3(NO_3)_3]$.

Bond distance (Å)		Bond angle (°)	
Eu–O1	2.472(2)	O1–Eu–O2	51.01(7)
Eu–O2	2.516(2)	O3–Eu–O4	51.17(6)
Eu–O3	2.522(2)	O5–Eu–O6	50.68(6)
Eu–O4	2.486(2)		
Eu–O5	2.477(2)	C–O7–Eu	143.8(2)
Eu–O6	2.550(2)	C–O8–Eu	152.0(2)
Eu–O7	2.360(1)	C–O9–Eu	134.4(2)
Eu–O8	2.322(1)		
Eu–O9	2.350(2)		
C–O7	1.265(3)		
C–O8	1.258(3)		
C–O9	1.286(4)		

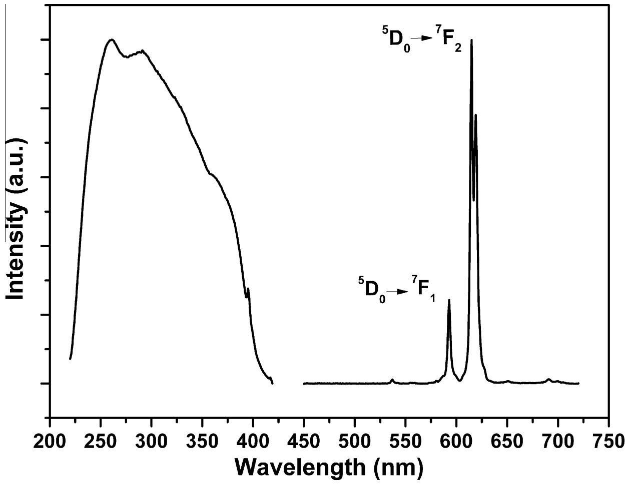

Fig. 4. Excitation (left) and emission spectrum of $[Eu(\mathbf{L})_3(NO_3)_3]$.

Table 3
Photophysical parameters for [Eu(L)$_3$(NO$_3$)$_3$].

τ_{exp} (ms)	τ_{rad} (ms)	Φ_{int} (%)	η_{sens} (%)	Φ_{tot} (%)
0.74	1.47	50	44	22

τ_{exp}: experimental lifetime, τ_{rad}: radiative lifetime, Φ_{int}: intrinsic quantum yield, η_{sens}: sensitization efficiency, Φ_{tot}: external photoluminescence quantum yield.

one of the nitrogen atoms prevents the bidentate coordination of the phenanthroline molecule, thus hindering the normal mode of coordination to the metal. Instead, the ligand binds to the lanthanoid ion *via* its ketone moiety. While bèta-diketones have been widely studied as sensitizing ligand for lanthanoid compounds, ketones generally are considered poor ligands and thus seem to get less attention. However, complexes of Eu(III) with Michler's ketone, benzophenone and azaxanthones have been studied and are reported to exhibit bright photoluminescence, with quantum yields in solution ranging from 9% to 24% [34–36].

4. Conclusion

1-Methyl-1,10-phenanthrolin-2(1*H*)-one has been synthesized from phenanthroline and used as a ligand for the first time, using Eu(III) as a central ion. The resulting complex is described by [Eu(**L**)$_3$(NO$_3$)$_3$] wherein the ligand is bound to Eu(III) in a monodentate fashion *via* its carbonyl oxygen. The complex exhibits strong photoluminescence characteristic of Eu(III) upon excitation in the ligand-centered band using near UV radiation. The quantum yield of this process is 22% indicating that the ligand is acting as a moderately effective antenna for Eu(III) luminescence, despite its unusual monodentate mode of binding to the metal ion. Further investigations on the use of substituted 1,10-phenanthrolines as a sensitizer have been performed and these results will be published in a future paper [18].

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Appendix A. Supplementary data

CCDC 918685 contains the supplementary crystallographic data for [Eu(**L**)$_3$(NO$_3$)$_3$]. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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