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ORIGINAL PAPER

Synthesis, Crystal Structures and Properties of Two Alkali-Lanthanide Heterometallic Coordination Polymers

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Abstract Synthesis, structure and properties of two alkali-lanthanide heterometallic coordination polymers with the stoichiometric formula $[M_5(OH)_4(H_2O)_{14}Ln(NO_3)_4]$ (where M is Na^+ and Ln, Er^{3+} or Yb^{3+}) are reported. They crystallize in the monoclinic $P2_1/c$ space group with very similar cell parameters: $a = 15.8777(19)$ Å, $b = 13.4173(18)$ Å, $c = 13.3515(17)$ Å, $\beta = 93.585(9)^\circ$, and $V = 2838.8(6)$ Å^3 for Er(III) and $a = 15.8756(5)$ Å, $b = 13.3707(4)$ Å, $c = 13.3083(4)$ Å, $\beta = 93.584(2)^\circ$, and $V = 2819.40(15)$ Å^3 for the Yb(III) polymer. The main findings in the structures of the new compounds are their isomorphism (due to the similarity between erbium and ytterbium ionic radii) and the coexistence in both of highly aqueous coordinated $[Na_5(OH)_4(H_2O)_{14}]^+$ and $[Ln(NO_3)_4]^-$ units. The luminescence measurements in the near infrared region after excitation at different wavelengths have confirmed the deleterious effect (quenching) of OH and H_2O groups on the emission (intensity and lifetime) of both erbium(III) and ytterbium(III) and the very weak optical absorption of lanthanides. Magnetic measurements show a paramagnetic behavior of the lanthanide centers.

Keywords Erbium(III) · Ytterbium(III) · Coordination polymer · Photoluminescence

Introduction

In the last 3 years visible-region organic light-emitting diode (OLED) technology has clearly shifted from the research and development phase to the scale-up phase, where primary concerns now deal with processing yields. In spite of the fact that the rapidly accelerating deployment of OLED displays in portable electronic devices indicate that many of the manufacturing issues are finally under control [1], fundamental science concerning the near infrared (NIR) emitters still remains to be resolved.

Most research efforts aimed at the development of such NIR-OLEDs have focused on lanthanide complexes. Despite the fact that direct optical excitation of the lanthanide ion is a low-efficiency process due to their weak optical absorption, it is known that the optical population of their emitting levels can be achieved by employing organic ligands as chromophores with strong absorption in the UV spectral region. These ligands can sensitize the central lanthanide ion by intramolecular energy transfer, a process known as "*antenna effect*" [2–7]. This motivated us to focus on a series of optically active complexes having the general formula [Ln(*β*-diketonate)$_3$(N,N-donor)] (Ln = Er, Yb), a wide family of materials intended for their use in the development of large area optoelectronic applications [8–10]. As a sub-product of these syntheses, it is frequent to find lanthanide hydroxynitrates, as the ones reported in this paper.

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Table 1 Crystal data and structure refinement of complexes

	Er(III) complex	Yb(III) complex
Empirical formula	$H_{32}ErN_4Na_5O_{30}$	$H_{32}N_4Na_5O_{30}Yb$
Formula weight	850.51	856.29
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	15.8777(19)	15.8756(5)
b (Å)	13.4173(18)	13.3707(4)
c (Å)	13.3515(17)	13.3083(4)
α (°)	90.00	90.00
β (°)	93.585(9)	93.584(2)
γ (°)	90.00	90.00
Volume (Å^3)	2838.8(6)	2819.40(15)
Z	4	4
Calculated density (g/cm^3)	1.990	2.017
Absorption coefficient (mm^{-1})	3.150	3.512
F(000)	1692	1700
Crystal size (mm^3)	0.30 × 0.13 × 0.11	0.24 × 0.21 × 0.18
θ range for data collection (°)	1.99–31.18	1.99–29.92
Index ranges	$-22 < h<23$, $-19 < k<19$, $-19 < l<19$	$-22 < h<22$, $-18 < k<18$, $-18 < l<18$
Reflections collected	40,994	63,344
Independent reflections [$I > 2\sigma(I)$]	7,439	5,665
Completeness to $2\theta = 51°$	98.4 %	99.7 %
Refinement method	Full matrix LS on F^2	Full matrix LS on F^2
Data/restrains/parameters	9047/36/469	8145/36/469
Goodness-of-fit on F^2	1.050	1.024
Final R indices [$I > 2\sigma(I)$]	$R = 0.0272$; w$R = 0.0611$	$R = 0.0343$; w$R = 0.0606$
R indices (all data)	$R = 0.0384$; w$R = 0.0652$	$R = 0.0738$; w$R = 0.0738$
Largest diff. peak and hole	−1.033/0.738	−1.250/1.408
CCDC number	942379	942380

A wide variety of double salts, e.g. $M_2Ln(NO_3)_5.nH_2O$, where M is ammonium or an alkali ion and Ln a trivalent lanthanide are known in the literature [11]. Moreover, hydroxynitrates, $Ln(OH)_2(NO_3)$ for La to Dy, with structures containing anion layers separating the $[Ln(OH)_2]^+$ polymeric cations have been characterized [12]. Nevertheless, alkali-lanthanide heterometallic coordination polymers are scarcer in the literature. This feature had led us to conduct their structural elucidation and characterize their properties.

Since OH groups and water molecules have been reported to be serious quenchers for the luminescence of any erbium or ytterbium materials [13], the study of the luminescence of the reported salts (rich in OH groups and highly hydrated) can exemplify, in a paradigmatic view, such behavior.

Lanthanides possess a high number of unpaired electrons, making them highly paramagnetic (effective magnetic moment of 9.60 μ_B for Er(III) and 4.50 μ_B for Yb(III), according to Hund's rules) and of special interest for applications such as NMR shift agents [14] or magnetic resonance imaging [15].

Experimental

Synthesis

$[Na_5(OH)_4(H_2O)_{14}Ln(NO_3)_4]$, where Ln is either Er(III) or Yb(III), were obtained as a sub-product of the synthesis of ternary complexes of lanthanides with β-diketonates and N,N-donors when excess sodium methylate or sodium hydroxide was used [16–19]. Crystals suitable for X-ray structure determination were grown from acetonitrile. Chemical formula: $H_{32}ErN_4Na_5O_{30}$ (MW: 850.51) and $H_{32}N_4Na_5O_{30}Yb$ (MW: 856.29). Anal. Calcd. for $H_{32}ErNa_5N_4O_{30}$: H, 3.79; Er, 19.67; Na, 13.52; N, 6.59; O, 56.44. Found. H, 4.12; Na, 14.05; N, 6.70. Anal. Calcd. for

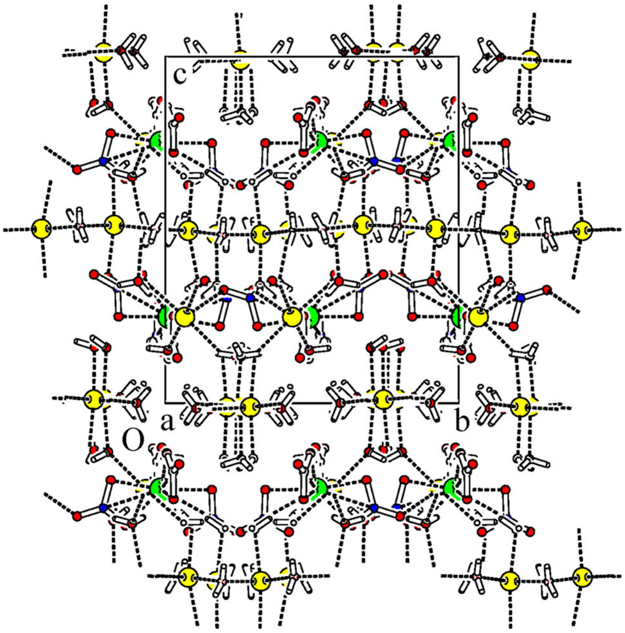

Fig. 1 Packing diagram of $[Na_5(OH)_4(H_2O)_{14}Ln(NO_3)_4]$ (Ln = Er, Yb) in the unit cell

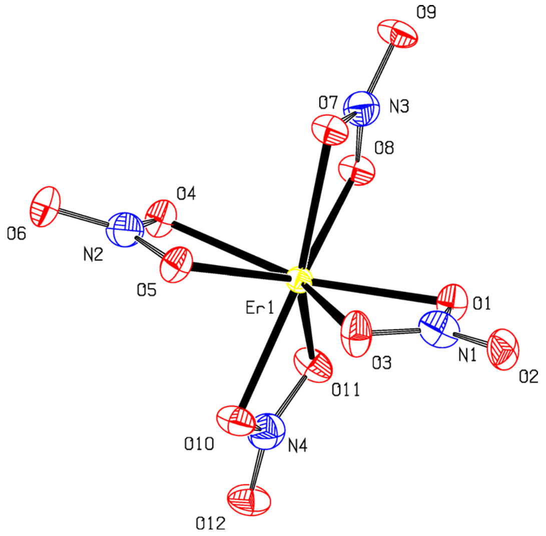

Fig. 2 Er(III) ion and its coordinating nitrate ions. *Ellipsoids* were drawn at the 50 % probability level

Table 2 Selected distances (Å) for the Ln(III) (Ln = Er, Yb) coordination environment

Bond	Er(III) complex	Bond	Yb(III) complex
Er1–O1	2.349(2)	Yb1–O1	2.318(3)
Er1–O3	2.334(2)	Yb1–O3	2.311(3)
Er1–O4	2.3610(19)	Yb1–O4	2.334(3)
Er1–O5	2.3287(19)	Yb1–O5	2.311(3)
Er1–O7	2.381(2)	Yb1–O7	2.364(3)
Er1–O8	2.3333(19)	Yb1–O8	2.313(3)
Er1–O10	2.3327(19)	Yb1–O10	2.301(3)
Er1–O11	2.364(2)	Yb1–O11	2.340(3)

$H_{32}YbNa_5N_4O_{30}$: H, 3.77; N, 6.54; O, 56-06; Yb, 20.21. Found: H, 3.85; N, 6.61.

Single-Crystal X-Ray Diffraction (SXD)

A Bruker Apex II CCD diffractometer (kappa geometry) was employed, using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Direct methods and conventional Fourier synthesis (SHELXS-97 [20]) were used to solve the structures and the refinement was made by full matrix least-squares on F^2 (SHELXL-97). All non-H atoms were refined anisotropically. The H atom positions could not be located in a difference Fourier synthesis, as it is usual in structures with heavy atoms. H atoms were placed in positions that maximized the H-bond interactions and refined fixing the distance to their parent O atoms (0.85 Å). Since it was impossible to distinguish between the hydroxo ions or the water molecules, each H atoms was assigned a 0.889 occupation. PLATON [21] was used for figure plotting (Table 1).

Photoluminescence Study

The photoluminescence emission spectrum of the compounds in NIR region (850–1,600 nm) was collected with a Jobin–Yvon FluoroLog-3 spectrofluorometer equipped with an InGaAs detector (liquid nitrogen cooled, range 0.8–1.6 μm) and a 450 W Xenon lamp, upon excitation at 350 nm. The spectrum was acquired with 1 s integration time at 1 nm step. The IR Stokes luminescence of the ytterbium compound was excited by an L-940/50/30 IR laser at 940 nm and was detected in the range 960–1,100 nm using an FPU-1 detector system and an upgraded monochromator for test and standard (L-54 phosphor) samples.

Magnetic Measurements

The magnetic susceptibility under several magnetic fields was measured with a S700X SQUID magnetometer (Cryogenic Ltd) in the temperature range 5–300 K and assuming a diamagnetic contribution of 2.208×10^{-4} emu/mol (estimated from tabulated Pascal constants).

Results

Crystal Structures

In tetradecaaqua-tetrahydroxo-pentasodium tetranitrato erbium(III) and ytterbium(III) (Fig. 1), the lanthanide ions occupy general positions, their coordination number is 8

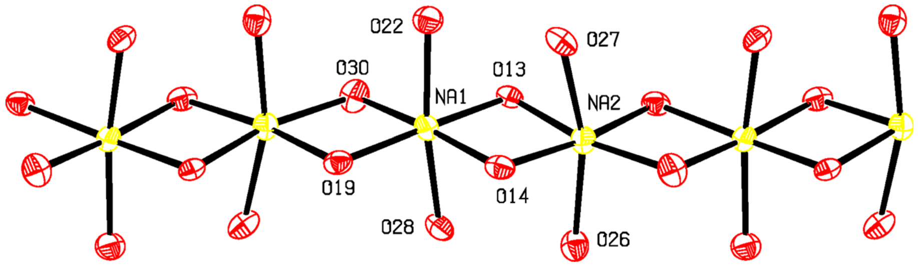

Fig. 3 One of the sodium chains that run along the *b* axis. *Ellipsoids* were drawn at the 50 % probability level

Table 3 Selected distances (Å) for the sodium coordination spheres

Bond	Na1	Bond	Na2	Bond	Na3	Bond	Na4	Bond	Na5
Er(III) complex									
Na1–O13	2.329(2)	Na2–O13	2.356(2)	Na3–O15	2.437(2)	Na4–O15	2.426(3)	Na5–O2	2.504(2)
Na1–O14	2.455(3)	Na2–O14	2.425(3)	Na3–O16	2.406(2)	Na4–O16	2.323(2)	Na5–O12	2.577(3)
Na1–O19	2.318(3)	Na2–O19	2.507(3)	Na3–O17	2.385(3)	Na4–O17	2.460(3)	Na5–O21	2.348(3)
Na1–O22	2.353(3)	Na2–O26	2.409(3)	Na3–O18	2.532(3)	Na4–O18	2.302(2)	Na5–O23	2.510(3)
Na1–O28	2.406(3)	Na2–O27	2.435(3)	Na3–O20	2.418(3)	Na4–O24	2.388(3)	Na5–O27	2.413(3)
Na1–O30	2.546(3)	Na2–O30	2.348(3)	Na3–O23	2.425(3)	Na4–O25	2.417(3)	Na5–O29	2.441(3)
Yb(III) complex									
Bond	Na1	Bond	Na2	Bond	Na3	Bond	Na4	Bond	Na5
Na1–O13	2.323(4)	Na2–O13	2.355(4)	Na3–O15	2.434(4)	Na4–O15	2.416(4)	Na5–O2	2.496(4)
Na1–O14	2.450(4)	Na2–O14	2.419(4)	Na3–O16	2.403(4)	Na4–O16	2.319(4)	Na5–O12	2.578(4)
Na1–O19	2.309(4)	Na2–O19	2.498(4)	Na3–O17	2.379(4)	Na4–O17	2.451(4)	Na5–O21	2.351(4)
Na1–O22	2.351(4)	Na2–O26	2.407(4)	Na3–O18	2.528(4)	Na4–O18	2.301(4)	Na5–O23	2.503(4)
Na1–O28	2.403(4)	Na2–O27	2.437(4)	Na3–O20	2.416(4)	Na4–O24	2.384(4)	Na5–O27	2.410(4)
Na1–O30	2.538(4)	Na2–O30	2.342(4)	Na3–O23	2.420(4)	Na4–O25	2.417(4)	Na5–O29	2.436(4)

Table 4 H bond parameters in Å and °

	Er(III) complex			Yb(III) complex		
	H···O	O···O	Angle	H···O	O···O	Angle
O13—H13A···O6[a]	1.94(3)	2.767(3)	166(4)	1.94(4)	2.765(4)	166(4)
O13—H13B···O3	1.90(3)	2.750(3)	172(3)	1.91(5)	2.756(5)	174(5)
O14—H14A···O6[b]	2.08(3)	2.930(3)	174(4)	2.10(5)	2.937(5)	178(6)
O14—H14B···O2[c]	2.16(3)	3.009(3)	177(4)	2.18(4)	3.015(5)	168(5)
O15—H15A···O9[d]	2.06(4)	2.902(3)	174(4)	2.06(5)	2.907(4)	172(5)
O15—H15B···O11	2.14(3)	2.968(3)	166(3)	2.14(4)	2.977(4)	169(5)
O16—H16A···O9[d]	1.95(3)	2.782(3)	168(4)	1.95(4)	2.782(4)	165(5)
O16—H16B···O11	1.95(3)	2.802(3)	173(3)	1.95(4)	2.800(4)	171(5)
O17—H17A···O21[d]	2.16(3)	2.978(4)	163(4)	2.14(5)	2.972(6)	164(5)
O17—H17B···O12	2.18(3)	2.987(3)	159(3)	2.16(4)	2.995(5)	166(6)
O18—H18A···O8[d]	2.05(4)	2.888(3)	176(3)	2.06(5)	2.891(4)	169(4)
O18—H18B···O8	2.01(3)	2.860(3)	178(4)	2.01(4)	2.855(4)	173(6)
O19—H19A···O5[b]	2.03(3)	2.878(3)	172(3)	2.03(5)	2.874(4)	170(6)
O19—H19B···O5	2.18(4)	3.020(3)	170(3)	2.19(5)	3.024(4)	171(5)
O20—H20A···O4	1.92(3)	2.760(3)	172(4)	1.90(6)	2.750(5)	172(7)
O20—H20B···O25	2.23(2)	3.017(4)	154(4)	2.22(3)	3.002(6)	153(6)
O21—H21A···O20[e]	2.016(14)	2.848(3)	166(5)	2.03(2)	2.845(6)	162(6)
O21—H21B···O9	1.902(13)	2.736(3)	167(5)	1.94(3)	2.726(5)	155(6)
O22—H22A···O2	2.085(18)	2.907(3)	162(5)	2.11(3)	2.900(6)	155(6)
O22—H22B···O7[c]	1.94(3)	2.773(3)	170(4)	1.92(6)	2.769(5)	176(7)
O23—H23A···O1[c]	1.94(4)	2.745(3)	159(3)	1.91(6)	2.752(5)	169(5)
O23—H23B···O24	2.009(19)	2.858(3)	176(5)	2.00(3)	2.848(6)	173(6)
O24—H24A···O1	1.87(3)	2.720(3)	172(4)	1.88(5)	2.712(5)	164(6)
O24—H24B···O9[c]	2.05(2)	2.872(3)	162(4)	2.08(4)	2.868(5)	154(6)
O25—H25A···O4[f]	2.06(4)	2.900(3)	173(4)	2.05(6)	2.898(5)	174(5)
O25—H25B···O12	2.038(15)	2.852(4)	161(4)	2.026(19)	2.843(5)	161(6)
O26—H26A···O7[a]	2.03(4)	2.854(3)	165(4)	2.01(5)	2.846(5)	170(5)
O26—H26B···O28	2.090(17)	2.899(4)	159(4)	2.13(3)	2.894(6)	149(6)
O27—H27A···O10	1.89(4)	2.704(3)	161(4)	1.89(5)	2.703(5)	161(5)
O27—H27B···O22	2.13(2)	2.943(4)	161(4)	2.10(3)	2.928(6)	164(5)
O28—H28A···O6[a]	2.08(2)	2.914(3)	167(5)	2.12(3)	2.908(5)	155(6)
O28—H28B···O10[b]	1.93(3)	2.772(3)	174(4)	1.93(5)	2.774(5)	171(6)
O29—H29A···O6[b]	1.917(19)	2.748(3)	166(5)	1.92(3)	2.746(5)	163(8)
O29—H29B···O26	2.040(13)	2.886(3)	172(5)	2.030(18)	2.879(6)	176(8)
O30—H30A···O29[g]	2.04(3)	2.883(4)	169(4)	2.06(5)	2.882(6)	160(5)

[a] 1 − x, −1 − y, 1 − z

[b] 1 − x, 1/2 + y, 1/2−z

[c] x, −1/2−y, −1/2 + z

[d] −x, −1 − y, 1 − z

[e] x, −3/2−y, 1/2 + z

[f] x, −3/2−y, −1/2 + z

[g] x, −1/2−y, 1/2 + z

and their coordination polyhedron is a distorted square antiprism. 8 oxygen atoms (from 4 nitrate ions) are in the immediate environment of the lanthanide ions (Fig. 2). The Ln(III)–O distances are in the range 2.32–2.38 Å for Er(III) and 2.30–2.36 Å for Yb(III), see Table 2. There are not common vertices in consecutive lanthanide polyhedra.

The sodium ions are coordinated by the water molecules, located at the vertices of octahedrons. Some of the water molecules coordinate to more than one ion. Na1 and Na2 ions are assembled in chains along b axis through the sharing of two coordinating oxygen atoms (Fig. 3), in the equatorial plane. A similar chain, with Na3 and Na4 ions, is assembled along the *a* axis.

In the coordination sphere of the remaining sodium ion (Na5) there are axial oxygen atoms from the two above described chains and also an oxygen atom from a nitrate group. Therefore all alkaline metal and lanthanide ions are bridged in a 3D network (Table 3).

A very intricate 3D H-bond network further links all ions together (Table 4; Fig. 4).

There are no solvent accessible voids in this structure.

Photoluminescence Spectra

After excitation at 350 nm for $[Na_5(OH)_4(H_2O)_{14}Er(NO_3)_4]$ (either in solid state or dissolved in D_2O) and under excitation at 980 nm for photoluminescence spectra for $[Na_5(OH)_4(H_2O)_{14}Yb(NO_3)_4]$ (in solid state), photoluminescence spectra were registered in comparison to other ternary complexes and standard samples. Both compounds gave poor NIR photoluminescence spectra with weak or unappreciable bands instead of the well-defined band of the reference samples (as it is illustrated in Fig. 5 for the Er(III) complex).

From the study of energy levels of vibrational modes, it can be clearly seen that OH^- groups are able to heavily quench lanthanide luminescence by deactivation of their emissive levels by vibronic coupling [13]. Thus, in Er^{3+}, the radiative transition in (~6500 cm^{-1}=1530 nm) between the ground state $^4I_{15/2}$ and the first excited state $^4I_{13/2}$, approximately matches the second harmonic of O–H bond vibrations (6,900 cm^{-1}). Hence, excited Er^{3+} ions can efficiently perturb the nearby O–H oscillators, resulting in a non-radiative transition. Therefore, the result of the study of Er^{3+} luminescence in the new alkali erbium hydroxynitrate, in which no Er^{3+} photoluminescence is observed in spite of the application of a high optical excitation power, is not surprising.

With regard to the analogous ytterbium compound, on the basis of previous works [22–24], Yb^{3+} IR luminescence quenching takes places as result of the mechanism reported by Zhang et al. [23]: excitation energy migration through Yb^{3+}–Yb^{3+} ions, followed by static energy transfer via dipole–dipole interaction between OH^- hydroxyl groups.

Magnetic properties

The variable-temperature magnetic susceptibilities for the erbium complex in the 5–300 K range at an applied field of 1 T is shown as a $1/\chi$ and $\chi_M T$ versus T plot in Fig. 6. The $\chi_M T$ values is 13.87 emu K mol^{-1} at room temperature, close to the expected value of 11.48 emu K mol^{-1} for one magnetic isolated Er(III) ion [25] (the difference may be attributed to impurities in the reagent). Upon lowering the temperature, the $\chi_M T$ value decreases continuously. The $1/\chi$ plot shows a linear behavior up to low temperatures. Both behaviors show a paramagnetic response of the Er(III) ion to the applied magnetic field.

The magnetization *versus* field has been measured at 5 K. Below 1 T it increases sharply and the slope is

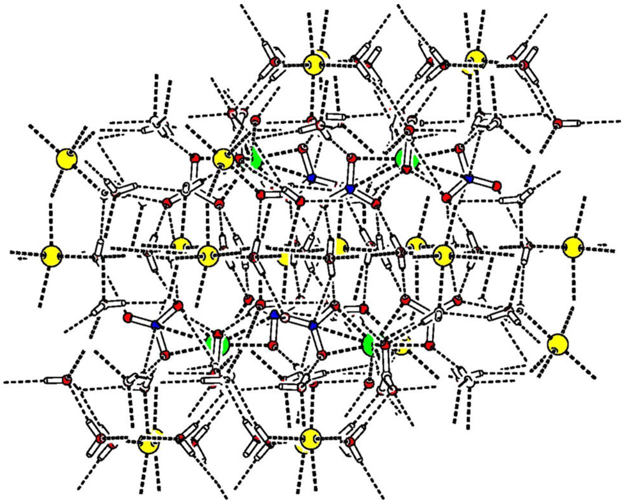

Fig. 4 H-bond network depicted as *dashed lines*

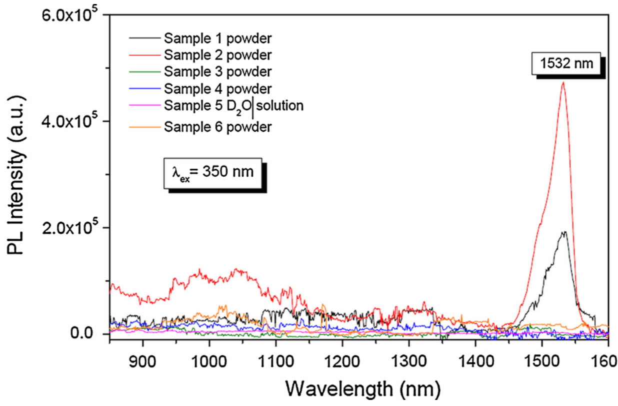

Fig. 5 PL spectra in NIR region (850–1,600 nm) with 350 nm excitation wavelength

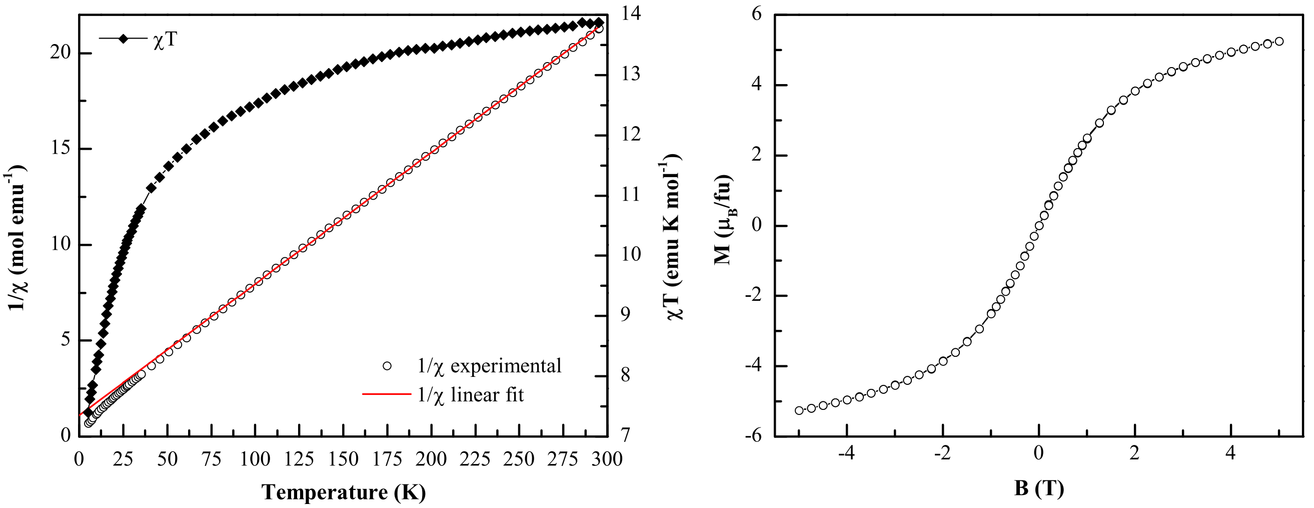

Fig. 6 1/χ and χ_MT vs. T (*left*) and M versus B (*right*) for the erbium(III) complex

steep. Above this field, the magnetization increases slowly, reaching a maximum value of 5.25 μ_B/fu at 5 T.

Supplementary Data

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 942379 and 942380. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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