Synthesis, crystal structures, luminescence and magnetic properties of lanthanide complexes containing the 1,8-bis(2-hydroxybenzamido)-3,6-dioxaoctane ligand

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The reaction of 1,8-bis(2-hydroxybenzamido)-3,6-dioxaoctane (**H_2L**) with lanthanide nitrates in MeCN afforded new binuclear lanthanide complexes (Ln = La–Nd, Sm–Yb or Y, **1**–**13**) in high yields, and the molecular structures of **1** and **2** were established by X-ray crystallography. A photophysical study of the ligand **H_2L** and of the binuclear complexes (Ln = Nd, Sm, Eu, Tb and Dy) has been performed and the quenching effect of coordinated water molecules was observed. The **H_2L** and Tb complex exhibit an up-conversion process under OPO excitation at 660 nm. The magnetic properties of Pr and Gd complexes are also reported.

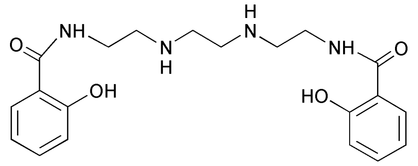
Over the past 40 years, the study of the coordination chemistry of lanthanides has been undertaken. In the early stages, studies of lanthanide salts or reactions with some small organic molecules were made.[1–6] Lanthanide ions are regarded as hard Lewis acids and show a strong coordination preference with hard bases such as F^- and H_2O. Macrocyclic ligands such as 1,4,7,10-tetraazacyclododecane (cyclen) are actively being studied in view of their potential applications in biomedical research.[7–11] Calixarenes have been exploited to give polytopic receptors for the complexation of trivalent lanthanide ions, either for extraction purposes, nuclear waste management or for the design of efficient lanthanide-based luminescent devices and probes.[12–15] Another type of ligand, acyclic polyethers, can be used in the extraction and analysis of rare earths.[16–18] The extraction of fission products by *N*,*N*,*N*′,*N*′-tetraphenyl-3,6,9-trioxaundecanediamide (TTD) has been studied using an isotopic tracer technique, and the extractability of alkaline earths and lanthanide ions with a nitrobenzene solution of TTD is very high when picrate is used as an accompanying ion.[19] These acyclic polyethers form lanthanide complexes such as $[Er(Pic)_3(TTD)]$[20] by coordinating the oxygen atoms of the polyethers and the amide. The IR analysis demonstrated that the metal binds more strongly to the amide oxygen than to the polyethers.

In the study of lanthanide complexes, the coordination chemistry of the early lanthanides is not well established[21] and most of the solid state structures have been obtained from the late lanthanide elements.[22] Detailed investigations have been mainly focussed on the luminescent and magnetic properties of Eu, Gd, Tb and Dy.[14,15,23] Recently, we reported the crystal structures and luminescent behaviour of tripodal amide systems, with early lanthanide elements, showing a strong interaction between the carbonyl oxygen and the metal centre.[24] Herein, we report the synthesis of a series of lanthanide complexes containing multidentate amide ligands, substituted with a hydroxy functional group in order to enhance its coordination ability and the solid state structure of two complexes with early lanthanide elements. Apart from the magnetic and photoluminescence properties that have been studied, a novel up-conversion phenomenon in the binuclear lanthanide complexes has also been investigated.

Experimental

Materials and syntheses

All solvents were purified and dried by standard methods prior to use.[25] All chemicals, unless otherwise stated, were purchased commercially and used as received. Ligand (**H_2L**) was prepared by literature methods.[26]



Ligand **H_2L**

$[La(\mu\text{-}OPhC_4H_8N_2O)_2(NO_3)_5(H_2O)_2(CH_3OH)][NO_3]\cdot H_2O\cdot MeOH$, 1, $[Ln(\mu\text{-}OPhC_4H_8N_2O)_2(NO_3)_4(H_2O)_4][NO_3]_2\cdot 2H_2O\cdot 4MeCN$ [Ln = Pr–Nd, Sm–Yb, Y (2–13)]. A solution of $Ln(NO_3)_3\cdot 6H_2O$ (0.25 g, 0.65 mmol) in acetonitrile (10 cm^3) was added to 1,8-bis(2-hydroxybenzamido)-3,6-dioxaoctane (**H_2L**; 0.25 g, 0.65 mmol) dissolved in MeCN (10 cm^3). The suspension was stirred at room temperature for 2 days. The mixture was filtered over Celite and washed with MeCN to obtain the product. Crystals were obtained by slow evaporation of an acetonitrile solution.

1: yield 84%. IR (KBr disc): ν 3401, 1609, 1470–1476, 1383, 1305–1310 cm^{-1}. Anal. found: C, 22.6; H, 2.7; N, 12.5%; calcd

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for $C_{21}H_{32}N_{10}O_{25}La_2$: C, 22.9; H, 2.9; N, 12.7%. Positive ion FAB MS: m/z 911 (calcd 910) $[La_2L(NO_3)_4]^+$.

2: yield 76%. IR (KBr disc): ν 3401, 1609, 1465–1469, 1383, 1300–1308 cm^{-1}. Anal. found: C, 21.5; H, 2.8; N, 12.4%; calcd for $C_{20}H_{32}N_{10}O_{26}Pr_2$: C, 21.6; H, 2.9; N, 12.6%. Positive ion FAB MS: m/z 915 (calcd 914) $[Pr_2L(NO_3)_4]^+$.

3: yield 65%. IR (KBr disc): ν 3395, 1615, 1470–1477, 1385, 1300–1308 cm^{-1}. Anal. found: C, 21.6; H, 2.7; N, 12.3%; calcd for $C_{20}H_{32}N_{10}O_{26}Nd_2$: C, 21.4; H, 2.7; N, 12.5%. Positive ion FAB MS: m/z 919 (calcd 920) $[Nd_2L(NO_3)_4]^+$.

4: yield 70%. IR (KBr disc): ν 3383, 1614, 1470–1477, 1385, 1300–1304 cm^{-1}. Anal. found: C, 21.0; H, 2.7; N, 12.2%; calcd for $C_{20}H_{32}N_{10}O_{26}Sm_2$: C, 21.3; H, 2.9; N, 12.4%. Positive ion FAB MS: m/z 934 (calcd 933) $[Sm_2L(NO_3)_4]^+$.

5: yield 68%. IR (KBr disc): ν 3395, 1614, 1470–1475, 1385, 1300–1309 cm^{-1}. Anal. found: C, 21.4; H, 2.9; N, 12.1%; calcd for $C_{20}H_{32}N_{10}O_{26}Eu_2$: C, 21.2; H, 2.8; N, 12.4%. Positive ion FAB MS: m/z 938 (calcd 936) $[Eu_2L(NO_3)_4]^+$.

6: yield 60%. IR (KBr disc): ν 3389, 1612, 1470–1473, 1385, 1300–1306 cm^{-1}. Anal. found: C, 21.2; H, 2.6; N, 12.3%; calcd for $C_{20}H_{32}N_{10}O_{26}Gd_2$: C, 21.0; H, 2.8; N, 12.3%. Positive ion FAB MS: m/z 948 (calcd 948) $[Gd_2L(NO_3)_4]^+$.

7: yield 74%. IR (KBr disc): ν 3389, 1616, 1470–1473, 1385, 1305–1310 cm^{-1}. Anal. found: C, 20.7; H, 2.7; N, 12.1%; calcd for $C_{20}H_{32}N_{10}O_{26}Tb_2$: C, 20.9; H, 2.8; N, 12.2%. Positive ion FAB MS: m/z 951 (calcd 950) $[Tb_2L(NO_3)_4]^+$.

8: yield 60%. IR (KBr disc): ν 3395, 1615, 1470–1477, 1385, 1300–1308 cm^{-1}. Anal. found: C, 20.8; H, 2.6; N, 12.0%; calcd for $C_{20}H_{32}N_{10}O_{26}Dy_2$: C, 20.8; H, 2.8; N, 12.1%. Positive ion FAB MS: m/z 959 (calcd 957) $[Dy_2L(NO_3)_4]^+$.

9: yield 60%. IR (KBr disc): ν 3364, 1614, 1470–1477, 1385, 1300–1304 cm^{-1}. Anal. found: C, 20.6; H, 2.6; N, 12.2%; calcd for $C_{20}H_{32}N_{10}O_{26}Ho_2$: C, 20.7; H, 2.8; N, 12.1%. Positive ion FAB MS: m/z 963 (calcd 962) $[Ho_2L(NO_3)_4]^+$.

10: yield 55%. IR (KBr disc): ν 3401, 1616, 1470–1479, 1385, 1305–1311 cm^{-1}. Anal. found: C, 20.5; H, 2.5; N, 11.9%; calcd for $C_{20}H_{32}N_{10}O_{26}Er_2$: C, 20.7; H, 2.8; N, 12.0%. Positive ion FAB MS: m/z 968 (calcd 966) $[Er_2L(NO_3)_4]^+$.

11: yield 53%. IR (KBr disc): ν 3407, 1618, 1470–1477, 1385, 1300–1308 cm^{-1}. Anal. found: C, 20.7; H, 2.9; N, 12.1%; calcd for $C_{20}H_{32}N_{10}O_{26}Tm_2$: C, 20.6; H, 2.7; N, 12.0%. Positive ion FAB MS: m/z 971 (calcd 970) $[Tm_2L(NO_3)_4]^+$.

12: yield 55%. IR (KBr disc): ν 3383, 1614, 1470–1477, 1389, 1300–1306 cm^{-1}. Anal. found: C, 20.6; H, 2.5; N, 11.7%; calcd for $C_{20}H_{32}N_{10}O_{26}Yb_2$: C, 20.5; H, 2.7; N, 11.9%. Positive ion FAB MS: m/z 980 (calcd 978) $[Yb_2L(NO_3)_4]^+$.

13: yield 54%. IR (KBr disc): ν 3401, 1609, 1465–1469, 1383, 1300–1308 cm^{-1}. Anal. found: C, 23.7; H, 3.4; N, 13.7%; calcd for $C_{20}H_{32}N_{10}O_{26}Y_2$: C, 23.9; H, 3.2; N, 13.9%. Positive ion FAB MS: m/z 811 (calcd 810) $[Y_2L(NO_3)_4]^+$.

Crystallography

Single crystals suitable for X-ray crystallographic analyses for complexes **1** and **2** were mounted in glass capillaries. Diffraction data were collected at room temperature on a Bruker AXS SMART CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Information concerning crystallographic data collection and structure refinements is summarised in Table 1. Intensity data were also corrected for Lorentz and polarisation effects and an approximation of absorption correction by inter-image scaling was also applied. Space groups of both crystals were determined from a combination of Laue symmetry checks and their systematic absences were confirmed by successful refinement of the structures. The structures were solved by direct methods: SIR 92[27] or SHELXS 86[28] along with Fourier-difference techniques. Structure refinements were made on F by full-matrix least-squares analysis. The hydrogen atoms of the organic moieties were generated in their idealised position. All calculations were performed on a Silicon-Graphics computer using the program package TEXSAN.[29]

Table 1 Crystal data and structure refinement for complexes **1** and **2**

	1	**2**
Empirical formula	$La_2C_{22}H_{38}N_{10}O_{27}$	$Pr_2C_{28}H_{48}N_{14}O_{28}$
Formula weight	1152.40	1310.58
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$ (#15)	$C2/c$ (#15)
a/Å	40.149(1)	22.760(1)
b/Å	12.072(1)	10.847(1)
c/Å	21.691(2)	21.550(1)
β/°	91.970(2)	106.83(2)
U/Å^3	10506(1)	5092.3(7)
Z	8	4
T/K	298.2	298.2
μ(Mo-Kα)/cm^{-1}	16.82	19.84
Reflections collected	31 479	17 167
Unique reflections	12 448	4639
Observed reflections [$I > 1.5\sigma(I)$]	6803	3342
R_{int}	0.04	0.03
R^a	0.066	0.048
wR^b	0.086	0.059

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

CCDC reference numbers 175401 and 175402. See http://www.rsc.org/suppdata/nj/b1/b108942c/ for crystallographic data in CIF or other electronic format.

Photophysical measurements

The luminescence spectra were recorded using a Perkin–Elmer LS 50B Luminescence spectrophotometer equipped with a R928 photomultiplier tube and the spectra were corrected for detector response and stray background light. Phosphorescence lifetimes were measured with the instrument in time-resolved mode, and are the average of at least three independent measurements made by monitoring the decay at a wavelength corresponding to the maximum intensity of the emission spectrum, following pulsed excitation. The resulting first-order decay curves gave linear ln I *vs.* t plots from which the lifetime was calculated by $\tau = 1/\text{slope}$. The up-conversion experiment was performed using an optical parametrical oscillator (OPO) system and it was precise enough to tune the appropriate wavelength for the excitation source or the scanning excitation measurement. A Nd:YAG laser (Quantel Brilliant B) was employed as the excitation light and was used to pulse the OPO (Ototek Magic Prism VIR) with a tunable range from 410 to 670 nm in the visible range. The line-width of the OPO is less than 0.1 nm at a wavelength of 420 nm, but it increases to 1.25 nm at 650 nm. **H_2L** and complex **7** were pulsed by a laser light source with a 4 ns pulse width.

Other measurements

Infrared spectra were recorded on a Bio-Rad FTS-7 IR spectrometer, from KBr pellets in the range 4000 to 400 cm^{-1}.

Mass spectra were recorded with a Finnigan MAT 95 instrument by the fast atom bombardment (FAB) technique using m-nitrobenzyl alcohol or α-thioglycerol as matrix solvents.

Variable temperature magnetisation characterisations were performed using a Quantum Design SQUID magnetometer equipped with a 5 Tesla magnet in the temperature range of 2 to 300 K. All data were corrected for diamagnetism.

Results and discussion

X-Ray crystallography

The reaction of hydrated lanthanide nitrates with **H_2L**, in a 1 : 1 ratio in acetonitrile, affords complexes **1**–**13** with satisfactory yields. Single crystals of **1** suitable for X-rays analysis were obtained from the slow evaporation of an acetonitrile solution at room temperature for a week. A perspective drawing of **1** and its selected bond parameters are shown in Fig. 1 and Table 2, respectively. A binuclear La complex is observed in the X-ray studies, having one ligand wrapped around the two metal ions. The coordination geometry of La(1) can be described as a bicapped square antiprism. This metal centre is ten-coordinated: three bidentate nitrate ions, a water molecule, and the oxygen atoms of an amide group and phenoxy group on the ligand **H_2L**. However, La(2) is nine-coordinated with a tricapped trigonal prism coordination geometry: two bidentate nitrate ions with one of them found to have positional disorder, one water and one methanol molecule, the oxygen atoms of the carbonyl group and phenoxy group on the ligand. The phenolate oxygens of the ligand bridge the two metal centres, with the bond distance of La(2)–O(2) being slightly longer than that of La(1)–O(2) by 0.047 Å. As the metal-to-carbonyl and metal-to-phenoxy bond distances do not show large variations, it is difficult to compare the bond strengths. The metal–metal separation of 4.12 Å is longer than the mean value (*ca.* 4.08 Å) of the La···La distance in complexes with a LaO_2La core in the tripodal Schiff base system.[30–33]

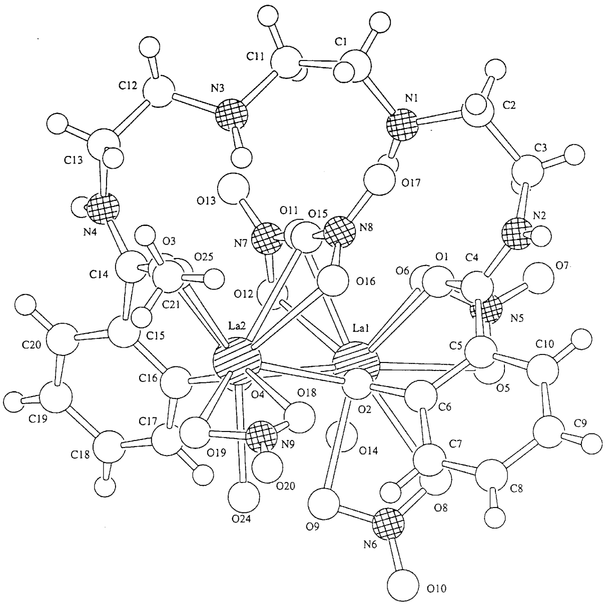

Fig. 1 The molecular structure of complex **1**.

Table 2 Selected bond distances (Å) and angles (°) for complex **1**

La(1)–O(1)	2.472(9)	La(2)–O(4)	2.460(9)
La(1)–O(2)	2.473(9)	La(2)–O(15)	2.728(9)
La(1)–O(4)	2.464(8)	La(2)–O(16)	2.740(10)
La(1)–O(5)	2.71(1)	La(2)–O(18)	2.7285(8)
La(1)–O(6)	2.70(1)	La(2)–O(19)	2.6970(9)
La(1)–O(8)	2.654(8)	La(2)–O(21)	2.6961(9)
La(1)–O(9)	2.748(9)	La(2)–O(22)	2.6372(8)
La(1)–O(11)	2.690(9)	La(2)–O(24)	2.623(10)
La(1)–O(12)	2.669(9)	La(2)–O(25)	2.59(1)
La(1)–O(14)	2.60(1)	La(1)–O(2)–La(2)	111.2(3)
La(2)–O(2)	2.520(8)	La(1)–O(4)–La(2)	113.5(3)
La(2)–O(3)	2.498(9)		

Pale green crystals of compound **2** suitable for diffraction analysis were also obtained from slow evaporation of an acetonitrile solution over a period of two weeks. The molecular structure of complex **2** with the atomic numbering scheme and its selected bond parameters are shown in Fig. 2 and Table 3, respectively. X-Ray analysis revealed that complex **2** is a binuclear Pr complex with one ligand wrapped around two metal centres, similar to complex **1**. However, this molecule contains a crystallographically imposed two-fold axis of symmetry passing through the mid-points of the metal-metal interaction and C(1)–C(1*), while the molecule of **1** is not symmetrical. Each Pr atom is nine-coordinated by two bidentate nitrate ions, two aquo ligands, and the oxygen atoms of an amide group and phenoxy group from the ligand. The metal geometry is essentially a tricapped trigonal prism. This coordination mode leads to considerable weakening of the C=O bond. In general, the stretching frequencies of C=O in the metal complexes are in the range of 1600–1620 cm^{-1}, whereas in the ligand it is 1636 cm^{-1}, as evident from the solid state (KBr disc) IR spectroscopic measurements. The binuclear complex is supported by extensive intramolecular hydrogen bonding. Interactions between the NH groups of the ligand and coordinated nitrate ions appear to hold the ligand assembly in a favourable conformation for metal coordination. In addition, extensive intermolecular hydrogen bonding is observed between coordinated water molecules, the polar NH groups of the ligand and the acetonitrile solvates.

Magnetic studies

The magnetic properties of complexes **2** and **6** in the solid state have been investigated at 5 Tesla and over the range of 2 to 300 K. The plots of χ_M^{-1} *vs.* T for **2** and **6** obey the Curie–Weiss law [$\chi = C/(T-\theta)$] with Weiss constants, θ, of −59.10

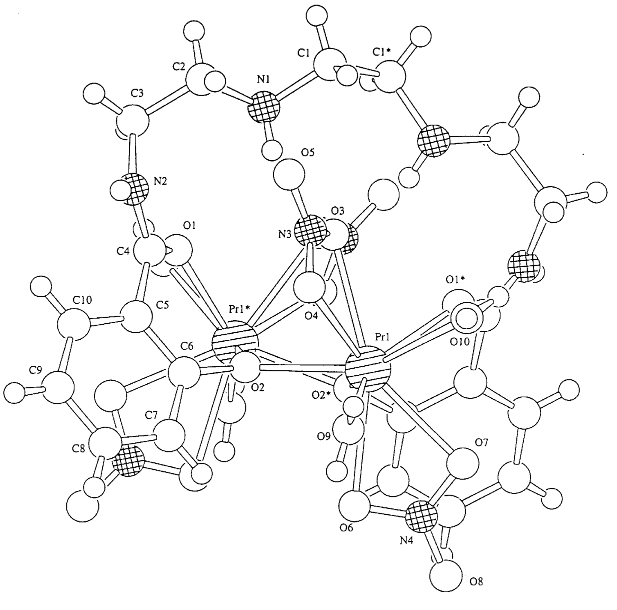

Fig. 2 The molecular structure of complex **2**.

Table 3 Selected bond distances (Å) and angles (°) for complex **2**

Pr(1)–O(1*)	2.442(4)	Pr(1)–O(9)	2.467(4)
Pr(1)–O(2)	2.388(4)	Pr(1)–O(10)	2.542(4)
Pr(1)–O(3)	2.622(4)	Pr(1*)–O(2)	2.429(4)
Pr(1)–O(6)	2.612(4)	Pr(1*)–O(4)	2.585(4)
Pr(1)–O(7)	2.529(4)	Pr(1)–O(2)–Pr(1*)	110.0(1)

and −2.66 K, respectively. The Curie constants of complexes **2** and **6** are 3.48 and 15.49 cm^3 K mol^{-1}, which are consistent with the theoretical value for dinuclear complexes of Pr and Gd (Pr: 3.20 cm^3 K mol^{-1}, Gd: 15.86 cm^3 K mol^{-1}). The variation of the magnetic susceptibility of complexes **2** and **6** is presented in Fig. 3 and 4, respectively, in the form of $\chi_M T$ *vs. T.* There is a continuous decrease in the value of $\chi_M T$ as the temperature is lowered from room temperature. For **2**, the $\chi_M T$ value per molecule is 3.04 cm^3 K mol^{-1} at room temperature and decreases continuously to a value of 0.11 cm^3 K mol^{-1} at 2 K. This indicates the presence of anti-ferromagnetic coupling between the Pr^{3+} ions and strong spin-orbital coupling in the dinuclear Pr^{3+} complex. For complex **6**, the $\chi_M T$ is equal to 15.52 cm^3 K mol^{-1} at 250 K and remains nearly constant from room temperature down to *ca.* 50 K, then decreases rapidly on further cooling, reaching a minimum value of 6.95 cm^3 K mol^{-1} at 2 K (Fig. 4). The dramatic decrease in the value of $\chi_M T$ at low temperatures is mainly attributed to the weak intra- and intermolecular anti-ferromagnetic coupling between the Gd^{3+} ions, and may also partially arise from the very small splitting of the $^8S_{7/2}$ multiplet at zero field, or additional splitting of the ground state multiplet promoted by a Gd^{3+}-Gd^{3+} interaction at low temperature, since the applied field is small. The irregularity observed at around 40 K is probably due to the presence of a trace of impurity.

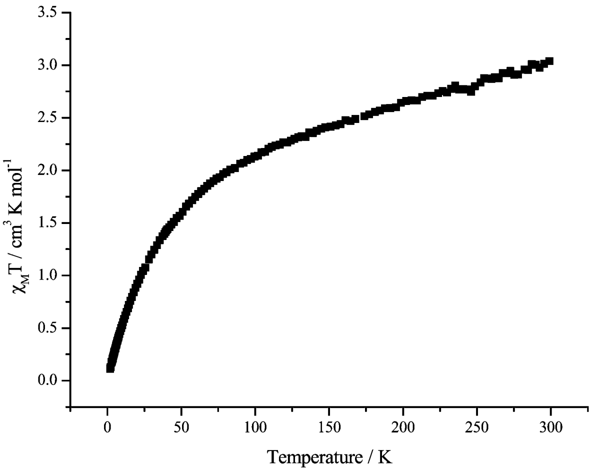

Fig. 3 Thermal dependence of $\chi_M T$ for complex **2**.

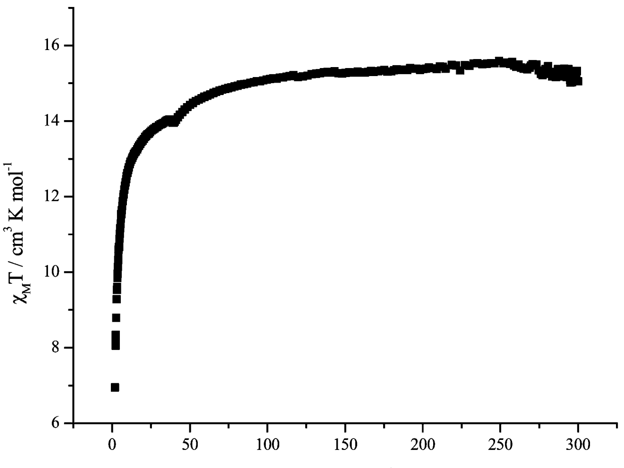

Fig. 4 Thermal dependence of $\chi_M T$ for complex **6**.

Photophysical studies

An absorption spectrum of **H$_2$L** in methanol exhibits an absorption maximum at 303 nm and, under the conditions of the photophysical measurements, a broad emission peak at 435 nm was observed. The luminescence measurements of complexes **3**–**5**, **7** and **8** were also conducted in the solid state at room temperature and a strong ligand-based emission at about 438 nm was found. Among the samples, only Nd, Tb and Dy complexes showed characteristic metal-based emissions with a relatively weak intensity. This may suggest that the energy transfer step of the ligand from the triplet excited state to the excited state of the metal ions is not efficient, thus resulting in very weak metal-based luminescence. As the solid state structure of the complexes possesses some coordinated water, it is suggested that the luminescence is quenched by the O–H oscillator.[34,35] Except for the Nd(III) complex, studies on the luminescent behaviour of the complexes were carried out in DMSO at room temperature. The overall luminescent intensity of the metal-based emission in solution is higher than that of the solid state. It is believed that the coordinated water molecules are displaced by the DMSO molecules, leading to a diminished quenching influence of the O–H oscillator. The occurrence of the ligand-based emission in the fluorescence spectra of metal complexes suggests that the energy transfer from the ligand to the metal centre is ineffective and cannot sensitise the metal emission to a large extent (Fig. 5–7). Within these complexes, it was found that the Eu(III) complex does not

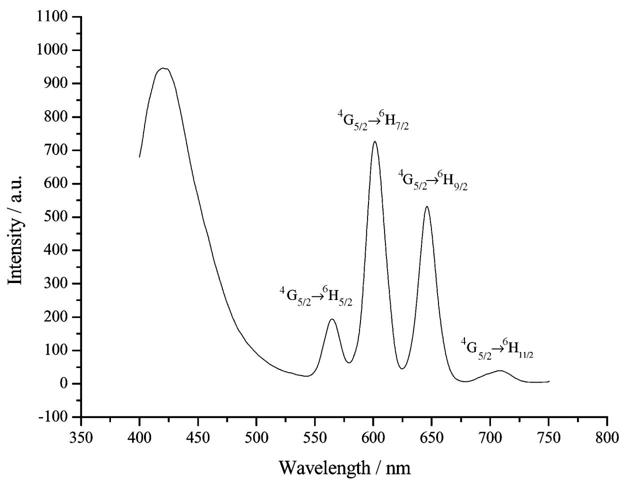

Fig. 5 Emission spectrum of the Sm complex **4** in DMSO.

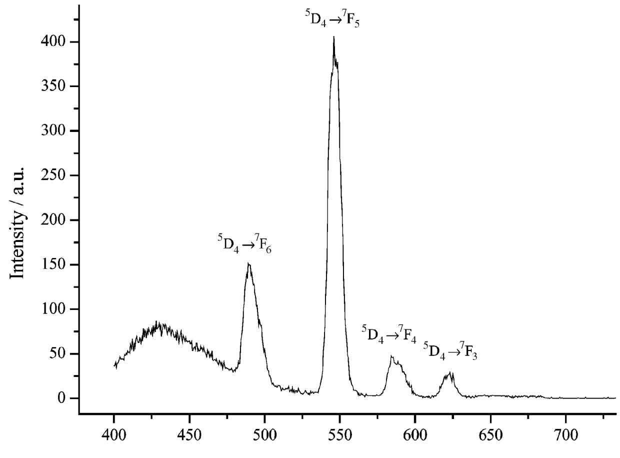

Fig. 6 Emission spectrum of the Tb complex **7** in DMSO.

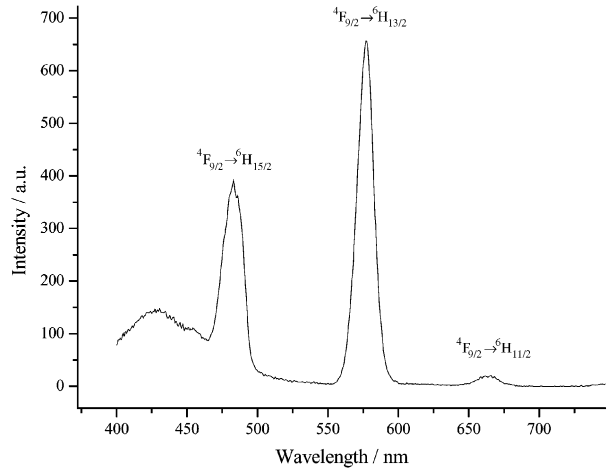

Fig. 7 Emission spectrum of the Dy complex **8** in DMSO.

show its characteristic structured emission; its luminescence is completely quenched by other deactivation pathways.[36]

The solid state photoluminescence of ligand **H$_2$L** and complex **7** were first measured with a 325 nm He-Cd laser as the excitation source. An emission peak at *ca.* 425 nm was observed in ligand **H$_2$L**; the occurrence of an unsymmetrical peak is probably due to the presence of more than one emissive centre in the ligand. The excitation spectrum was performed by monitoring the emission peak with the use of a 400 nm filter. The profile of the curve with an onset starting at 270 nm was obtained. For the Tb complex, apart from the metal-based luminescence peaks at 490, 545, 586 and 623 nm, which correspond to the transitions of $^5D_4\rightarrow{}^7F_6, {}^7F_5, {}^7F_4$, and $^7F_3$, respectively, a ligand emission was also observed. The inefficient energy transfer from ligand to metal excited state may lead to the existence of ligand emission, Fig. 8. The excitation spectrum of the complex is similar to that of the ligand, with a profile of the curve onsets at 275 nm. Both ligand and metal excitation are observed for the complex.

The up-conversion measurement was made with an optical parametric oscillator (OPO) system with a tunable range from 410 to 670 nm in the visible range. By using an OPO operating at 660 nm as the excitation source, a ligand emission at *ca.* 425 nm was observed, that is an emission of higher energy is found in **H$_2$L** when using a lower excitation energy, hence an up-conversion process in **H$_2$L** was detected. The up-conversion photoluminescence excitation was also measured; the profile started at about 560 nm, in which the energy of the excitation was approximately half of the normal photoluminescence excitation value. Similarly, metal-based luminescence is also revealed in complex **7** with the use of an OPO at 660 nm (Fig. 9), with the up-conversion excitation profile of the curve again starting at 560 nm. Interestingly, there is no ligand emission (or only extremely weak emission) in the spectrum of the complex. This may suggest that once the first photon is pumped up, some non-radiative pathways from the metastable state may compete with adsorption of the second photon. Hence, the new excited state, which has a different energy the original one, may be close to the emitting level of Tb^{3+}. Therefore, it is believed that the energy transfer from ligand to metal is more efficient, and as a result, a metal-based luminescence is observed.

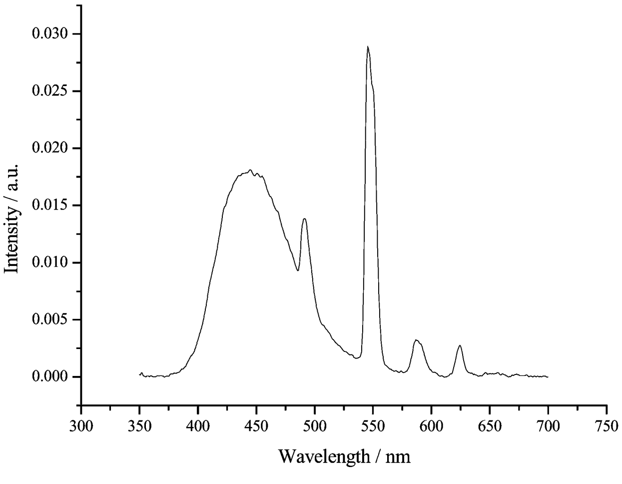

Fig. 8 The luminescence spectrum of complex **7** at 10 K with He–Cd 325 nm radiation as excitation source.

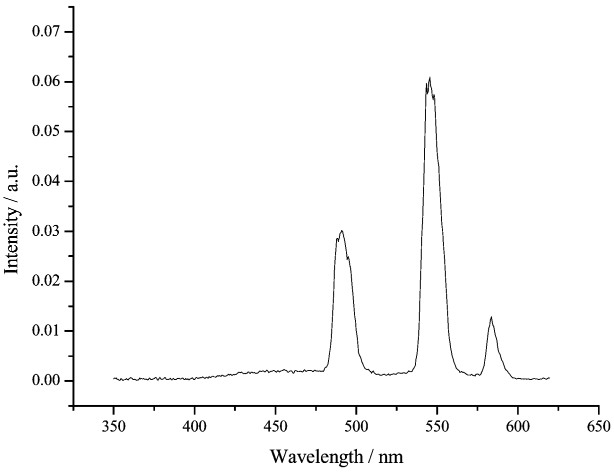

Fig. 9 The up-conversion photoluminescence spectrum of complex **7** at 10 K with an OPO at 660 nm.

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