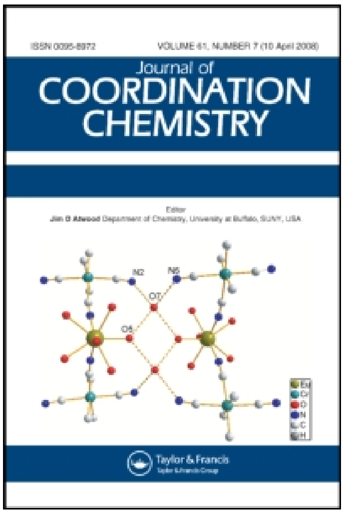

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Synthesis and crystal structure of yttrium(III) and lanthanide(III) complexes with a new terpyridine-like ligand 2,4-*bis*(3,5-dimethylpyrazol-1-yl)- 6-diethylamino-1,3,5-triazine

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SYNTHESIS AND CRYSTAL STRUCTURE OF YTTRIUM(III) AND LANTHANIDE(III) COMPLEXES WITH A NEW TERPYRIDINE-LIKE LIGAND 2,4-*bis*(3,5-DIMETHYLPYRAZOL-1-YL)-6-DIETHYLAMINO-1,3,5-TRIAZINE

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A new planar aromatic tridentate terpyridine-like ligand, 2,4-*bis*(3,5-dimethylpyrazol-1-yl)-6-diethylamino-1,3,5-triazine (L), has been synthesized and the structures of its complexes [$YL(NO_3)_3$] (**1**) and [$LnL(NO_3)_3(H_2O)$]L [Ln = La (**2**), Ce (**3**), Pr (**4**), Nd (**5**), Eu (**6**)] have been determined by X-ray crystal structural analysis. The structures of the five lanthanoid complexes are isomorphous and isostructural but different from the crystal structure of the yttrium complex [$YL(NO_3)_3$]. The latter shows a nine-coordinate metal center whereas the crystal structure of the lanthanoid complexes [$LnL(NO_3)_3(H_2O)$]L show a 10-coordinate metal center. The π–π stacking and hydrogen bonding between the coordinated and uncoordinated L molecules sensitized the Ln luminescence. The thermal behavior of the ligand and its complexes is discussed.

Keywords: Terpyridine-like ligand; Lanthanoid complexes; Yttrium complex; Crystal structure; Luminescence

INTRODUCTION

Terpyridine and terpyridine-like compounds have attracted considerable interest because of their extensive coordination chemistry with metal ions [1–15]. The particular molecular chelating structure of the terpyridine and terpyridine-like chromophores enables them to form not only photo- and redox-active complexes with transition-metal ions as catalysts [4–7] but also highly luminescent complexes with lanthanoid ions as probes in biology and medicine [9–13]. Even the bis-terpyridine complexes of iridium(III) exhibit luminescence sensitive to chloride at physiologically relevant concentrations [8]. In addition, separation of trivalent lanthanides from actinides in acidic aqueous solutions from nuclear fuel reprocessing by liquid extraction continues to be a challenge [16]. By synergistic extraction, terpyridine and terpyridine-like

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compounds can give high values of separation factors for actinides over lanthanides [14].

As lanthanoid complexes exhibit diverse and unpredictable structural variations in both coordination number and coordination geometry, entire isomorphous and isostructural lanthanoid series are rarely characterized structurally. The design and development of highly luminescent lanthanide complexes are of increasing interest. With suitable chromophoric ligands, luminescent lanthanide complexes may be formed in which the chromophoric ligands absorb energy and then transfer it effectively to the lanthanide cations, or shield the lanthanide cations from interaction with solvent molecules, which leads to deactivation of the luminescent excited state [17,18]. Terpyridine and terpyridine-like compounds that can form extensive conjugated systems by coordination to a metal cation may act as such ligands. With careful modification of the ligands, the luminescence intensity can be enhanced [9]. Among these terpyridine and terpyridine-like compounds are 2,6-*bis*(2-pyridyl)pyridine [5–8,14], 2,6-*bis*(benzimidazol-2-yl)pyridine [4,12], 2,6-*bis*(5-butyl-1,2,4-triazol-3-yl)pyridine [15], 2,6-*bis*(3,5-dimethylpyrazol-1-ylmethyl)pyridine [3], 2,6-*bis*(pyrazol-1-yl)pyridine [1], 2,4,6-*tris*(3,5-dimethylpyrazol-1-yl)-1,3,5-triazine [10], 2,4-*bis*(3,5-dimethylpyrazol-1-yl)-6-methoxy-1,3,5-triazine [2,11] and 2,4-*bis*(3,5-dimethylpyrazol-1-yl)-6-amino-1,3,5-triazine [14]. These compounds generally fall into two groups, one with pyridine-centered ligands, and the other with 1,3,5-triazine-centered ligands. We report here a new 1,3,5-triazine-centered ligand, 2,4-*bis*(3,5-dimethylpyrazol-1-yl)-6-diethylamino-1,3,5-triazine (*L*), the crystal structures of its complexes with Y^{III}, La^{III}, Ce^{III}, Nd^{III} and Eu^{III} and their luminescent properties.

EXPERIMENTAL

Physical Measurements and Materials

IR spectra (400–4000 cm^{-1}) were recorded on a Perkin-Elmer FTIR1750 spectrophotometer with KBr pellets. Elemental analyses (C, H, N) were carried out on a Carlo-Erba 1106 elemental analyzer. Solvents and starting materials were used as commercial grade without further purification. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Thermal analyses were carried out with a Rigaku thermal analyzer in air from room temperature to 700°C.

Synthesis of 2,4-*bis*(3,5-Dimethyl-l-pyrazolyl)-6-diethylamino-1,3,5-triazine (*L*)

8 mL of triethylamine containing about 11% diethylamine was added dropwise whilst stirring at room temperature to a mixture of 3,5-dimethylpyrazole (3.84 g, 0.04 mol) and 2,4,6-trichloro-1,3,5-triazine (1.844 g, 0.01 mol) in acetone (40 mL). The solution was refluxed for 4 h and then filtered. The filtrate was evaporated to dryness, and the residue was recrystallized in methanol to give 3.2 g of product *L*, yield 90.8% (based on 2,4,6-trichloro-1,3,5-triazine); m.p. 126–145°C. Anal. Calcd. for $C_{17}H_{24}N_8 \cdot H_2O$(%): C, 56.98; H, 7.26; N, 31.28. Found: C, 56.72; H, 7.21; N, 31.16. ^{1}H NMR δ (ppm): 1.253 (t, 6H), 3.674 (q, 4H), 2.336 (s, 6H), 2.692 (s, 6H), 6.029 (s, 2H).

Preparation of the Complexes

All complexes were obtained by the general synthetic method as follows: to a stirred solution of *L* (0.3 mmol) in methanol (3 mL) was added dropwise a solution of lanthanide nitrate (0.1 mmol) in methanol (2 mL). The solution was stirred for 30 min and then filtered. The filtrate was left to stand undisturbed at room temperature. After several weeks, X-ray-quality crystals were obtained.

Crystallography

Intensity data were collected at room temperature on a Raxis-iv X-ray diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) in the ω–2θ scan mode. Details of the crystal structure solution and refinement are presented in Table I. The structures were solved by the direct method and refined by full-matrix least-squares on F^2. All nonhydrogen atoms were refined with anisotropic thermal parameters while hydrogen atoms were included but not refined. Structure solution and refinement were performed using the SHELXL-97 crystallographic software package [19]. Selected bond length and angles are shown in Table II.

RESULT AND DISCUSSION

Synthesis of the Ligand

When attempting to prepare 2,4,6-tris(3,5-dimethyl-l-pyrazolyl)-1,3,5-triazine by reaction of 3,5-dimethylpyrazole with 2,4,6-trichloro-1,3,5-triazine in acetone in the presence of triethylamine, ligand *L* separated (Scheme 1), as determined by NMR. This was later confirmed to result from the triethylamine used, which was contaminated by diethylamine (about 11% diethylamine determined by GC). It seemed that the reaction of 2,4,6-trichloro-1,3,5-triazine was much easier with diethylamine than with 3,5-dimethylpyrazole. To get a better yield of *L*, a slight excess of diethylamine in triethylamine was added to the reaction mixture. When potassium carbonate was used as acid absorbent, 2,4,6-tris(3,5-dimethyl-l-pyrazolyl)-1,3,5-triazine could be obtained.

Crystal Structure

The structure of complex **1**, $[YL(NO_3)_3]$, is shown in Fig. 1. The yttrium atom is nine-coordinate to three nitrogen atoms from a single tridentate ligand *L*, and six oxygen atoms from three bidentate NO_3 groups. In this structure, *L* shows signs of steric strain in complexing to the metal. The average distance between the yttrium atom and the coordination nitrogen atoms is 2.465 Å. There are two kinds of directions in its layered packing structure (Fig. 2). Every other layer is parallel and the dihedral angle of every adjacent layer is 43.5°.

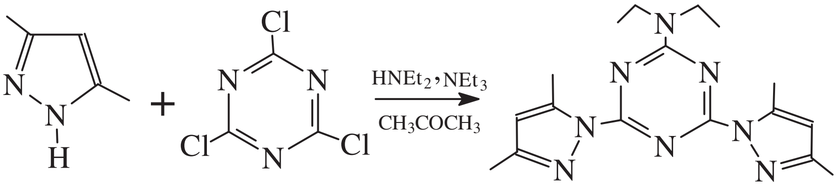
By contrast, complexes **2**–**6**, $[LnL(NO_3)_3 \cdot (H_2O)]L$ [Ln = La (**2**), Ce (**3**), Pr (**4**), Nd (**5**), Eu (**6**)], are isomorphous and isostructural, with each crystal in the *P*-1 space group, and composed of neutral $[LnL(NO_3)_3 \cdot (H_2O)]$ molecules and uncoordinated

TABLE I Crystal data and structure refinement for Complexes **1**–**6**

	1	***2***	***3***	***4***	***5***	***6***
Empirical formula	$C_{17}H_{24}N_{11}O_9Y$	$C_{34}H_{50}LaN_{19}O_{10}$	$C_{34}H_{50}CeN_{19}O_{10}$	$C_{34}H_{50}PrN_{19}O_{10}$	$C_{34}H_{50}NdN_{19}O_{10}$	$C_{34}H_{50}EuN_{19}O_{10}$
Formula weight	615.38	1023.84	1025.05	1025.84	1029.17	1036.89
Temperature (K)	291	293	291	291	291	291
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*2(1)/*n*	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1
a (Å)	12.519(3)	12.504(3)	12.511(3)	12.471(3)	12.453(3)	12.387(3)
b (Å)	12.561(3)	17.727(4)	17.740(4)	17.720(4)	17.778(4)	17.871(4)
c (Å)	16.171(3)	11.806(2)	11.799(2)	11.788(2)	11.781(2)	11.773(2)
α (°)	90	107.91(3)	107.89(3)	107.81(3)	107.93(3)	108.02(3)
β (°)	93(3)	114.49(3)	114.46(3)	114.53(3)	114.40(3)	114.37(3)
γ (°)	90	77.09(3)	77.38(3)	77.61(3)	77.82(3)	77.99(3)
Volume ($Å^{-3}$)	2537.5(9)	2252.0(8)	2255.7(8)	2244.8(8)	2249.4(8)	2247.8(8)
Z	4	2	2	2	2	2
D_c ($g\,cm^{-3}$)	1.611	1.510	1.509	1.518	1.519	1.532
Absorption coefficient (mm^{-1})	2.367	1.023	1.083	1.160	1.229	1.470
F(000)	1256	1048	1050	1052	1054	1060
Θ range (°)	2.00–27.52	1.21–27.65	1.21–27.53	1.21–27.55	1.21–27.57	1.20–25.00
Reflections collected/unique	7597/4611	6694/6694	7360/7360	7358/7358	6704/6704	6784/6784
R(int)	0.0516	0.0000	0.0000	0.0000	0.0000	0.0000
Data/restraints/ parameters	4609/0/344	6687/0/578	7360/0/578	7358/0/568	6704/2/578	6781/2/578
F^2	1.134	1.230	0.110	1.025	1.090	1.108
R_1/wR_2	0.0628/0.1082	0.1066/0.3536	0.0518/0.1267	0.0496/0.1286	0.0663/0.1684	0.0467/0.1256
R indices (all data)	0.0923/0.1194	0.1200/0.3738	0.0610/0.1319	0.0583/0.1338	0.0787/0.1774	0.0510/0.1343

TABLE II Selected bond lengths (Å) and bond angles (°) for complexes **1**–**6**

Complex ***1***							
Y(1)–N(5)	2.435(3)	Y(1)–N(1)	2.469(4)	Y(1)–N(7)	2.490(4)	N(5)–y(1)–N(1)	64.41(12)
Y(1)–O(3)	2.463(4)	Y(1)–O(6)	2.414(3)	Y(1)–O(7)	2.461(4)	N(5)–y(1)–N(7)	63.98(11)
Y(1)–O(9)	2.376(4)	Y(1)–O(1)	2.383(4)	Y(1)–O(4)	2.403(3)	N(1)–y(1)–N(7)	128.29(11)
Complex ***2***							
La(1)–N(5)	2.708(13)	La(1)–N(1)	2.69(2)	La(1)–N(7)	2.684(14)	N(7)–La(1)–N(5)	58.5(4)
La(1)–O(3)	2.601(14)	La(1)–O(6)	2.627(14)	La(1)–O(7)	2.669(14)	N(1)–La(1)–N(5)	58.2(4)
La(1)–O(9)	2.584(15)	La(1)–O(1)	2.568(13)	La(1)–O(4)	2.598(14)	N(7)–La(1)–N(1)	115.5(4)
La(1)–O(10)	2.491(13)						
Complex ***3***							
Ce(1)–N(5)	2.683(4)	Ce(1)–N(1)	2.703(5)	Ce(1)–N(7)	2.660(5)	N(5)–Ce(1)–N(7)	59.12(14)
Ce(1)–O(3)	2.567(5)	Ce(1)–O(6)	2.544(4)	Ce(1)–O(7)	2.576(4)	N(1)–Ce(1)–N(5)	59.30(14)
Ce(1)–O(9)	2.565(4)	Ce(1)–O(1)	2.606(4)	Ce(1)–O(4)	2.660(3)	N(1)–Ce(1)–N(7)	117.30(14)
Ce(1)–O(10)	2.470(4)						
Complex ***4***							
Pr(1)–N(5)	2.653(5)	Pr(1)–N(1)	2.692(5)	Pr(1)–N(7)	2.651(5)	N(1)–Pr(1)–N(5)	59.60(14)
Pr(1)–O(3)	2.545(5)	Pr(1)–O(6)	2.564(4)	Pr(1)–O(7)	2.633(4)	N(5)–Pr(1)–N(7)	59.84(14)
Pr(1)–O(9)	2.534(4)	Pr(1)–O(1)	2.587(4)	Pr(1)–O(4)	2.545(5)	N(1)–Pr(1)–N(7)	118.36(14)
Pr(1)–O(10)	2.436(5)						
Complex ***5***							
Nd(1)–N(5)	2.631(7)	Nd(1)–N(1)	2.672(7)	Nd(1)–N(7)	2.633(1)	N(7)–Nd(1)–N(5)	60.2(2)
Nd(1)–O(3)	2.535(6)	Nd(1)–O(6)	2.538(6)	Nd(1)–O(7)	2.630(6)	N(7)–Nd(1)–N(1)	119.0(2)
Nd(1)–O(9)	2.530(6)	Nd(1)–O(1)	2.570(4)	Nd(1)–O(4)	2.515(6)	N(5)–Nd(1)–N(1)	60.0(2)
Nd(1)–O(10)	2.437(5)						
Complex ***6***							
Eu(1)–N(5)	2.570(5)	Eu(1)–N(1)	2.644(5)	Eu(1)–N(7)	2.604(5)	N(5)–Eu(1)–N(7)	60.89(15)
Eu(1)–O(3)	2.616(5)	Eu(1)–O(6)	2.481(5)	Eu(1)–O(7)	2.491(5)	N(5)–Eu(1)–N(1)	61.17(15)
Eu(1)–O(9)	2.545(5)	Eu(1)–O(1)	2.480(4)	Eu(1)–O(4)	2.507(4)	N(7)–Eu(1)–N(1)	120.97(15)
Eu(1)–O(10)	2.397(4)						



SCHEME 1.

ligand L molecules, where Ln is ten-coordinated with three nitrogens atoms from L, six oxygens from three bidentate NO_3 groups and one water molecule. Using $[LaL(NO_3)_3 \cdot (H_2O)]L$ as an example (Fig. 3), the coordinated L is almost planar with only small dihedral angles between the triazine and pyrazole rings (< 6.1°) and adopts a *cis–cis* conformation leading to a planar meridinal coordination of the Ln^{III}, which lies approximately in a basal plane defined by three coordinated nitrogen atoms of the L and the oxygen atom [O(1)] of a nitrate group. The uncoordinated ligand is connected to the coordinated water molecule through hydrogen bonding. The coordinated and uncoordinated ligands are packed in an AABB array running along the *b*-axis and packed in ABAB parallel layers running along the *c*-axis producing slipped stacks of the aromatic ligands with a zigzag arrangement (Fig. 4).

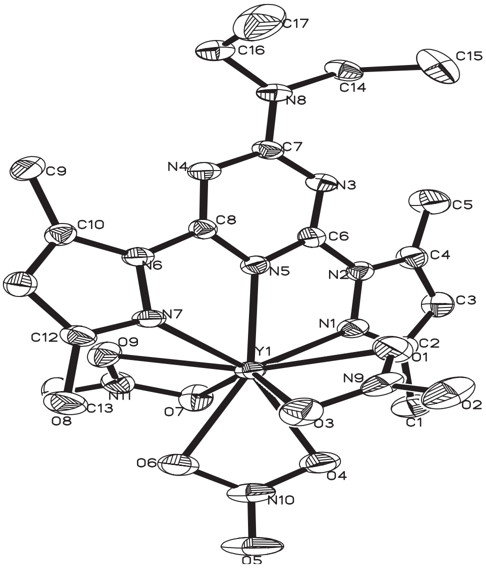


FIGURE 1 Molecular structure of Complex **1** [YL(NO_3)$_3$].

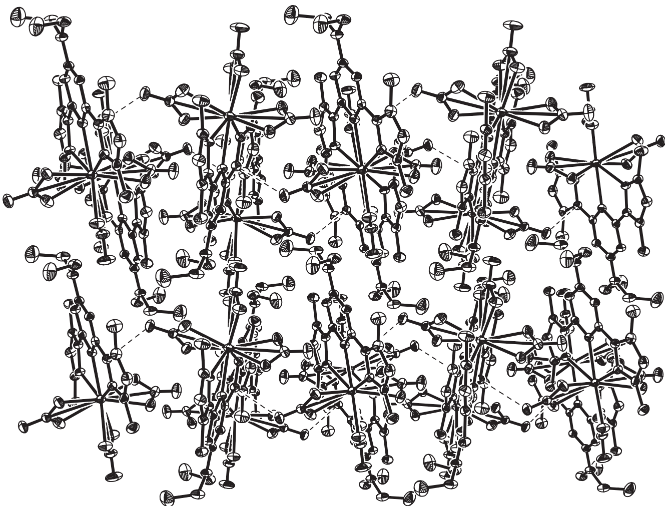


FIGURE 2 Molecular packing of Complex **1** [YL(NO_3)$_3$].

The metal–nitrogen bonds of these lanthanide complexes show consistent values with differences due to decrease in metal size.

By comparison to literature reports, the YL complex has a similar structure to the YbL' complex [L' = 2,6-bis(5-methyl-1,2,4-triazol-3-yl)pyridine], while the lanthanide complexes LnL [Ln = La, Ce, Pr, Nd, Eu] are similar to the LnL' [Ln = Nd, Sm, Tb] complexes [15], and almost the same as Eu complexes of 2,4-bis(3,5-dimethylpyrazol-1-yl)-6-methoxy-1,3,5-triazine [11] and 2,4,6-tris(3,5-dimethylpyrazol-1-yl)-1,3,5-triazine [10].

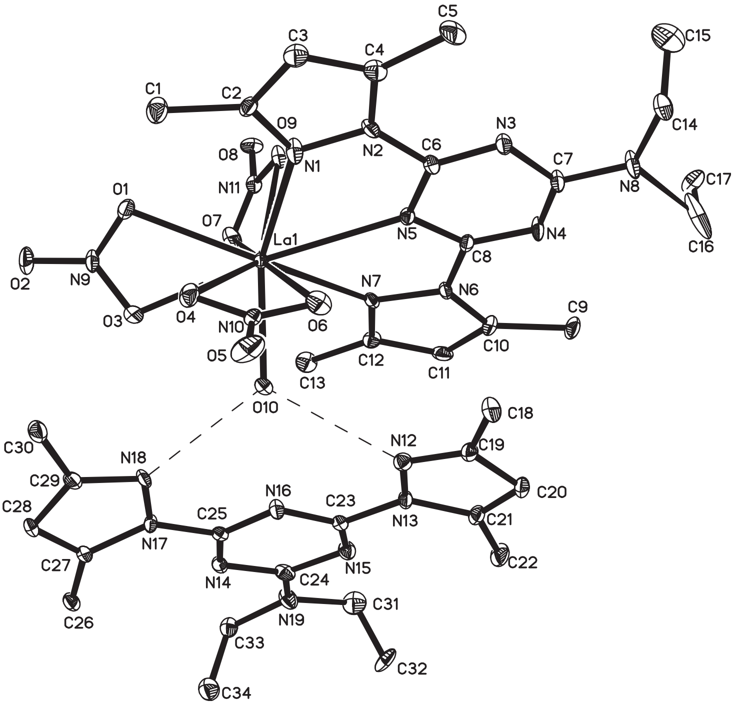


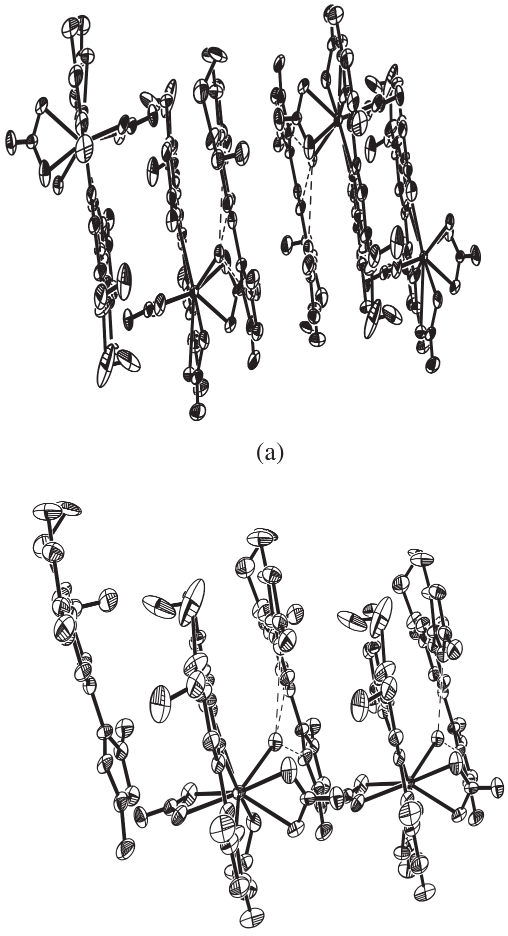
FIGURE 3 Molecular structure of Complex **2**.

IR Spectra

Selected IR data for the ligand and complexes **1**–**6** are given in Table III. The bands at 3429 cm^{-1} in the ligand are associated with O–H stretching, indicating the existence of crystal water, in agreement with the elemental analysis. Complexes **2**–**6** also gave bands at 3420–3432 cm^{-1}, indicating the existence of water. Bands characteristic of the free ligand ring-vibrations ($\nu_{C=N}$ and $\nu_{C=C}$ stretching) were observed as strong sharp peaks at 1600, 1519 and 1404 cm^{-1}. In the complexes, the bands characteristic of the ligand for the $\nu_{C=N}$ and $\nu_{C=C}$ stretching can also be observed as three strong sharp peaks but with some changes in the maximum absorbance, and the intensities are stronger and the peaks broadened. This may result from coordination of nitrogen atoms in the triazine ring and in the pyrazole rings to the lanthanide ions, as seen in the crystal structures. No free ligand ring-vibration could be observed in the complexes, which may be covered by the broadened and intensity-enhanced bands of the coordinated ligand. All complexes gave the absorption peaks of coordinated nitrate ions at 1285–1302 and 1352–1363 cm^{-1} [20], in agreement with the crystal structure determination.

Thermoanalyses

TG-DTA data for the ligand and its complexes were determined in air and are presented in Table IV. There is an endothermic peak at 100°C on the TG curves of the ligand with a weight loss of 5.1%, corresponding to the loss of one crystal water.



(a)

(b)

FIGURE 4 Molecular packing of Complexes **2**–**6** in (a) an AABB array running along the *b*-axis and (b) ABAB parallel layers running along the *c*-axis.

TABLE III Selected IR data (cm^{-1}) for the ligand and its complexes, **1**–**6**

Compound	$\nu_{O\text{–}H}$	$\nu_{C=N}$, $\nu_{C=C}$	ν_{NO_2} (*coordinate*)
L	3429s	1600s, 1519s, 1404s	–
Y*L*(NO_3)$_3$ (**1**)	3420m	1632s, 1507bs, 1440s	1285m, 1363m
La*L*(NO_3)$_3$ · (H_2O) (**2**)	3423m	1613s, 1492bs, 1430s	1297m, 1352m
Ce*L*(NO_3)$_3$ · (H_2O) (**3**)	3424m	1616s, 1479bs, 1432	1301m, 1352m
Pr*L*(NO_3)$_3$ · (H_2O) (**4**)	3432m	1621s, 1477bs, 1434s	1301m, 1353m
Nd*L*(NO_3)$_3$ · (H_2O) (**5**)	3423m	1616s, 1479bs, 1432s	1301m, 1353m
Eu*L*(NO_3)$_3$ · (H_2O) (**6**)	3426m	1618s, 1476bs, 1434s	1302m, 1354m

L decomposes between 220 and 612°C with two weak exothermic peaks. The yttrium complex has a consistent weight loss at 332–656°C with three exothermic peaks at 332, 390 and 504°C, and the total weight loss is 82.5%. Thus the residue is Y_2O_3. Complexes **2**–**6** have similar thermal behavior, losing water at 156–184°C

TABLE IV Thermal data for the ligand and its complexes

Complex	*Exothermic peak* (°C)	*Endothermic peak* (°C)	*Decomposition interval* (°C)	*Total weight loss* (%) (*calc.*)
L	231w, 321w	100	211–612,	97.8 (100)
$[\mathrm{Y}L(\mathrm{NO}_3)_3]$	332s, 390w, 504m		332–656	82.5 (81.6)
$[\mathrm{La}L(\mathrm{NO}_3)_3(\mathrm{H}_2\mathrm{O})]L$	464w, 407m, 428m, 476s	184	232–642	81.2 (84.1)
$[\mathrm{Ce}L(\mathrm{NO}_3)_3(\mathrm{H}_2\mathrm{O})]L$	328m, 429s	156	272–440	80.3 (84.1)
$[\mathrm{Pr}L(\mathrm{NO}_3)_3(\mathrm{H}_2\mathrm{O})]L$	320s, 368w, 504m	168	320–548	81.0 (84.0)
$[\mathrm{Nd}L(\mathrm{NO}_3)_3(\mathrm{H}_2\mathrm{O})]L$	312m, 400m, 482s	173	260–675	81.1 (83.7)
$[\mathrm{Eu}L(\mathrm{NO}_3)_3(\mathrm{H}_2\mathrm{O})]L$	270m, 410m, 460s, 540w	157	256–592	80.9 (83.0)

TABLE V Emission data and their assignments

Complex	λ_{ex} (nm)	λ_{em} (nm)[a]	*Assignment*
L	258	341, 358	
$[\mathrm{Y}L(\mathrm{NO}_3)_3]$	244	483	Ligand
$[\mathrm{La}L(\mathrm{NO}_3)_3(\mathrm{H}_2\mathrm{O})]L$	299	382	Ligand
$[\mathrm{Ce}L(\mathrm{NO}_3)_3(\mathrm{H}_2\mathrm{O})]L$	244	393	Ligand
$[\mathrm{Pr}L(\mathrm{NO}_3)_3(\mathrm{H}_2\mathrm{O})]L$	237	376	Ligand
$[\mathrm{Nd}L(\mathrm{NO}_3)_3(\mathrm{H}_2\mathrm{O})]L$	244	370	Ligand
$[\mathrm{Eu}L(\mathrm{NO}_3)_3(\mathrm{H}_2\mathrm{O})]L$	242	585 (0.178)	$^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_0$
		594 (0.241)	$^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_1$
		613 (1.000)	$^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_2$
		645 (0.035)	$^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_3$
		683 (0.036)	$^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_4$

[a] Relative intensities are given in parentheses.

with a weak endothermic peak, and decomposing between 232 and 675°C with two, three or four exothermic peaks, resulting in the final products of metal oxides. These results show that the complexes are more thermally stable than the parent ligand.

Luminescence Spectra

The luminescence spectra of the ligand and its complexes were recorded for powdered solids at room temperature. the emission data and their assignments are summarized in Table V. The results indicate that only the $\mathrm{Eu^{III}}$ complex exhibits strong luminescence, although all the complexes exhibit luminescence of the ligand by excitation at *ca* 244 nm.

Luminescence spectra of complex **5** are shown in Fig. 5. Excitation at the ligand-based $\pi \rightarrow \pi^*$ transition (239 or 294 nm) gives a characteristic $^5D_0 \rightarrow {}^7F_j$ emission of $\mathrm{Eu^{III}}$ but no ligand emission band, indicative of a fast intermolecular energy transfer from uncoordinated L to central $\mathrm{Eu^{III}}$. Methanol solution of **5** gives the same luminescence pattern as in the solid state, indicating that the intermolecular energy transfer of free ligand to the central europium ion arises from hydrogen bonding interactions found in the crystal of complex **5**, as intermolecular π–π stacking in the crystals no longer exists in solution. The observed $^5D_0 \rightarrow {}^7F_0$ and the intense hypersensitive

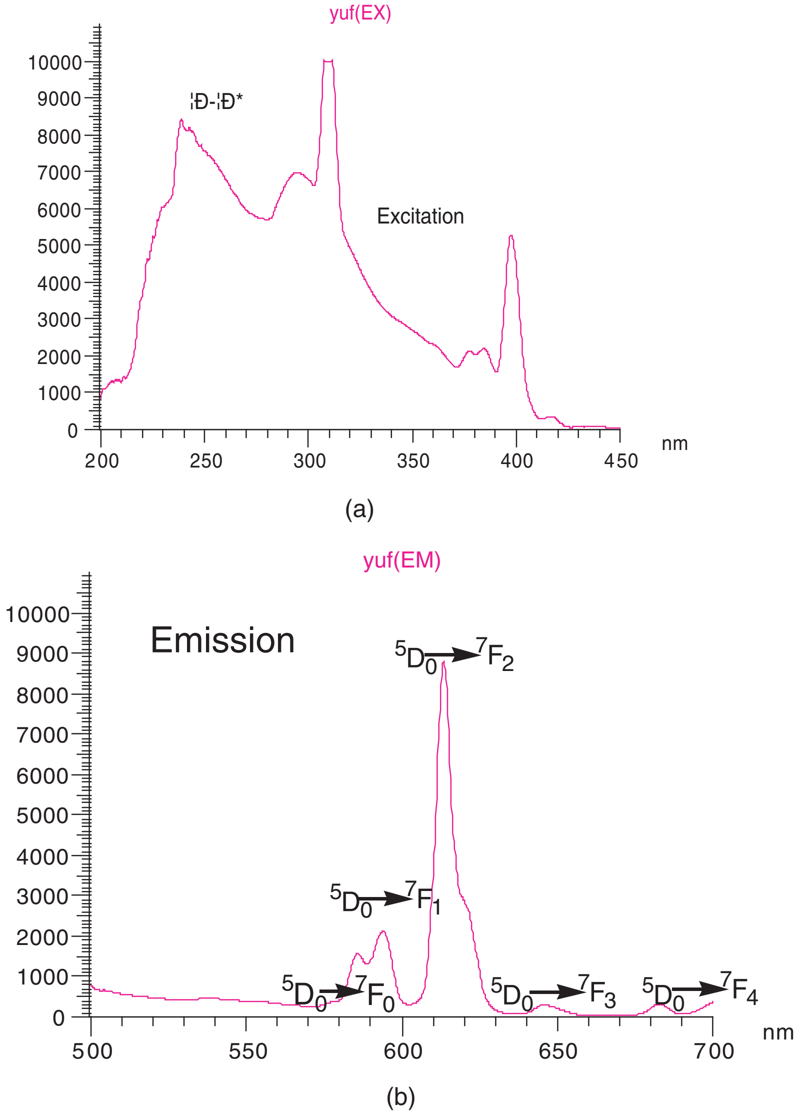


FIGURE 5 Luminescence spectra of **5**, $[EuL(NO_3)_3 \cdot (H_2O)]L$, in the solid state: (a) excitation; (b) emission.

$^5D_0 \rightarrow {}^7F_2$ transition reflect the low site symmetry of the europium ion [10,20,21], in agreement with the crystal structure.

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