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Synthesis and characterization of lanthanide complexes with a pentadentate triazine-based ligand

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Abstract: A series of mononuclear $[Ln(L)(H_2O)(NO_3)(solv)]$ ·solv, $(Ln = Pr (1), Nd (2), Sm (3), Eu (4), Gd (5), Tb (6-6a), Dy (7); solv = DMF, DMSO, H_2O) and L = 2,4-Bis(2-hydroxybenzylidenehydrazino)-6-methoxy-$ *s*-triazine complexes were prepared. The lanthanide(III) ions are nine-coordinated in the complexes and are bound to the O atoms of bidentate nitrate, three N and two O atoms of a pentadentate L ligand and one O atom from water and one O atom from dimethylformamide with a spherical capped square antiprism coordination environment in 1-7. The compounds have been characterized by means of elemental analysis, IR spectroscopy, UV-vis spectroscopy, X-ray diffraction, and thermal analysis. Lanthanide-centered emission of the complexes is overlapped by the ligand emission.

Keywords: Lanthanide complexes, Triazine ligands, X-ray structure, Optical properties

1. Introduction

The research on lanthanide(III) complexes have attracted attention in recent years due to their well-defined spectroscopic and magnetic properties [1-5]. The rare earth RE³⁺ ions are potential local luminescent probes for diagnostic application in biological systems [6-8]. RE³⁺ based compounds are highly promising building blocks for preparation of a single-molecule and single-chain magnets [9, 10]. Many other potential applications in areas as diverse as catalysis, optics, magnetic resonance imaging (MRI) have been reported [11-13].

Chlorinated derivative of *s*-1,3,5-triazine called cyanuric chloride ($C_3N_3Cl_3$) and its derivatives are currently intensively studied heterocyclic compounds with interesting biological qualities for pharmaceutical industry, mainly antifungal, antibacterial, antimalaric and antineoplastic [14-16]. By simple substitution of chlorine atoms in cyanuric chloride, using controlled conditions

(temperature) and different nucleophiles, various 2,4,6-mono, di- and trisubstituted, symmetrical and non-symmetrical derivatives bearing different substituents can be prepared [17]. Cyanuric chloride has temperature-dependent differential reactivity for displacement of chlorides with nucleophiles during S_NAr as shown in reaction Scheme 1 [18].

Please insert Scheme 1 here

Cyanuric chloride reacts efficiently with hydrazine hydrate to give mono-, di- or tri- substituted hydrazo- derivatives [19]. Several hydrazo-*s*-triazine derivatives have already been prepared and thoroughly studied [20, 21]. *s*-Triazine derivatives are of considerable current interest in coordination chemistry and supramolecular chemistry [22]. 2,4,6-trisubstituted-triazine derivatives proved their great potential in the field of material chemistry, both for their π -interaction abilities and for their aptitude to be involved in intricate H-bond networks [23].

Lanthanides in their trivalent state form complexes with strongly chelating ligands containing highly electronegative donor atoms [24, 25]. The ligands may have potential qualities to be applied in solvent extraction procedures of lanthanides and actinides as presented in several published papers, where similar triazine-based ligands were used [26-30]. These developments have inspired us to pursue the study which involves the systematic variation of different substituents on 2,4,6-trisubstituted-1,3,5-triazine. By condensation of aromatic aldehydes with 2,4-bis(hydrazino)-6-(S)-1,3,5-triazine, we already prepared a new, highly versatile group of pentadentate chelating agents which we have used to obtain uranyl(VI) complexes [31]. This work represents a continuation of the study with a focus on RE^{3+} lanthanide ions. Finally, we have synthesized a L ligand exhibiting high affinity to RE^{3+} ions.

Here we report the synthesis, structural characterizations and optical properties of eight lanthanide(III) coordination compounds $[Pr(L)(H_2O)(NO_3)(DMF)] \cdot DMF$ (1), $[Nd(L)(H_2O)(NO_3)(DMF)] \cdot DMF$ $[Sm(L)(H_2O)(NO_3)(DMF)] \cdot DMF$ (2),(3), [Eu(L)(H₂O)(NO₃)(DMF)]·DMF [Gd(L)(H₂O)(NO₃)(DMF)]·DMF (4), (5), [Tb(L)(H₂O)(NO₃)(DMF)]·DMF (6), $[Tb(L)(H_2O)(NO_3)(DMSO)] \cdot 2H_2O$ (6a), $[Dy(L)(H_2O)(NO_3)(DMF)] \cdot DMF(7) (L = C_{18}H_{17}N_7O_3).$

2. Experimental

2.1. Reagents and techniques

 $Dy(NO_3)_3 \cdot H_2O$, $Pr(NO_3)_3 \cdot 6H_2O$, $Sm(NO_3)_3 \cdot 6H_2O$, $Eu(NO_3)_3 \cdot 5H_2O$, $Gd(NO_3)_3 \cdot 6H_2O$, $Tb(NO_3)_3 \cdot 6H_2O$, $Nd(NO_3)_3 \cdot 6H_2O$ (Sigma-Aldrich), N,N-Dimethylformamide (Sigma-Aldrich, 98%), cyanuric chloride (Aldrich, 99%), hydrazine hydrate (Sigma-Aldrich, 50-60%), sodium bicarbonate (Sigma-Aldrich), methanol (Sigma-Aldrich, anhydrous, 99.8%), tetrahydrofuran (Sigma-Aldrich, anhydrous, 99.9%) and dimethyl sulfoxide (Sigma-Aldrich, anhydrous, 99.9%) were commercially available and were used without further purification.

FT-IR spectra were recorded using ATR technique by ALPHA FT-IR spectrometer (Bruker) in the 4000 - 400 cm⁻¹ region. The reported FT-IR signal intensities were defined as w = weak, m = medium and s = strong.

UV-vis absorption spectra of ligands and complexes were recorded using a Shimadzu UV-1602 spectrophotometer or GBC Scientific Equipment Cintra 2020 spectrophotometer in 1-cm quartz cuvette. The fluorescence emission spectra were performed on a FLS 920 fluorescence spectrometer (Edinburgh instruments) equipped with a 450 W Xe lamp and PMT detector with a double grating monochromator for both the excitation and the emission. Florescence spectra of the ligand and complexes were recorded upon excitation wavelength around their absorption maximum; spectra were collected from three repetitions. The measurements were performed in 1-cm fluorescence cuvettes in front face-geometry arrangement [31]. Elemental analysis (C, H and N) were performed using Elementar Vario EL III.

Diffraction data were collected on a Rigaku MicroMax-007 HF rotating anode CCD diffractometer using Mo K α radiation at 120 K. The structures were solved by direct methods and refined using the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (ShelXTL) [32]. A summary of the crystallographic data and structure refinement parameters is given in Table 4. The molecular graphics as well as additional structural calculations were drawn and interpreted using Diamond, ver. 3.2 (http://www.crystalimpact.com/diamond/Default.htm).

Thermal analysis (TG/DSC) was recorded on a Netzsch STA 449C Jupiter apparatus from 30 to 1000 °C under flowing synthetic air (70 cm³.min⁻¹) with a heating rate of 5 K min⁻¹. Powder diffraction patterns were collected with the PANalytical X'Pert PRO diffractometer equipped with conventional X-ray tube (Cu K α radiation, 40 kV, 30 mA) and a linear position sensitive detector PIXcel with an anti-scatter shield. Qualitative analysis was performed with HighScorePlus software package (PANalytical, The Netherlands, version 4.1.0), and Match3 (http://www.crystalimpact.com/match/Default.htm).

2.2. Synthesis of ligand L

The synthetic pathways to obtain intermediate and final compounds are shown in Scheme 2.

Stage 1: Cyanuric chloride (13.0 g, 70 mmol) was added into a solution of sodium bicarbonate (6.5 g, 77 mmol) in methanol (100 ml) at 10 $^{\circ}$ C and the resulting suspension was stirred for 1 h at room temperature. Solid white product was removed by filtration. Dry product was recrystallized from hot hexane to give 2,4-dichloro-6-methoxy-*s*-triazine (**DCMT**) in 85% isolated yield.

Stage 2: **DCMT** (10.05 g, 55.56 mmol) was suspended in tetrahydrofuran (200 ml) and stirred vigorously for 10 min. One portion of hydrazine hydrate (11.5 g, 0.227 mol) was added at room temperature and stirred for 1 h. After that, the mixture was refluxed for additional 12 h. The solution was cooled at room temperature. Cold distilled water was added into the solution and the

precipitated product was collected by filtration and dried to obtain pure **DHMT** (2,4-Bishydrazino-6-methoxy-*s*-triazine) powder in 70% isolated yield.

Stage 3: A reaction sequence according to Scheme 2 for L: DHMT (1.37 g, 8 mmol) was dissolved in 200 mL of anhydrous tetrahydrofuran and salicylaldehyde was added in one step (L) (1.95 mL, 16 mmol). The solution was heated under reflux overnight. After cooling the solution to room temperature, the crude product was obtained as a white powder.

For L (white powder): Yield: 31%. Anal. Calc. for $C_{18}H_{17}N_7O_3$ (379.37): C, 56.99; H, 4.52; N, 25.84%. Found: C, 56.78; H, 4.61; N, 25.69%. IR (ATR, v/cm⁻¹): v = 3568 (w); 2915 (w); 1618 (s); 1574 (s); 1516 (s); 1479 (s); 1366 (s); 1268 (m); 1156 (m); 951 (w); 799 (m); 742 (s).

Please insert Scheme 2 here

2.2. Synthesis of complexes 1-7

[Pr(L)(H₂O)(NO₃)(DMF)]·DMF (1). A suspension of L (379.4 mg; 1 mmol) in DMF (30 mL) was heated for 10 min. Then, solid Pr(NO₃)₃·6H₂O (434 mg; 1 mmol) was slowly added to the mixture under continuous heating and stirring to give a yellow solution. After 10 min of heating, Et₃N (1.51 mL; 1.5 mmol) was added dropwise and the mixture was heated for further 15 min. The resulting solution was stirred for 1 h and subsequently filtered. The yellow filtrate was left to evaporate slowly over three weeks, giving brown-yellow crystals suitable for X-ray diffraction analysis. The needle crystals were collected by filtration, washed with methanol and diethyl ether, and dried in air. Yield: 53%. Anal. Calc. $C_{24}H_{31}N_{10}O_9Pr$ (744.50): C, 38.55; H, 4.18; N, 18.73%. Found: C, 37.95; H, 3.58; N, 18.44%. IR (ATR, v/cm⁻¹): v = 3216 (w); 2925 (w); 1647 (m); 1603 (m); 1540 (s); 1466 (s); 1382 (m); 1379 (m); 1293 (m); 1198 (m); 1144 (w); 804 (m); 735 (m).

The syntheses of complexes 2-7 followed the procedure described for complex 1.

 $[Nd(L)(H_2O)(NO_3)(DMF)]$ ·DMF (2). Brown-yellow crystals. Yield: 47%. Anal. Calc. $C_{24}H_{31}N_{10}O_9Nd$ (747.83): C, 38.72; H, 4.20; N, 18.81%. Found: C, 38.34; H, 3.78; N, 18.59%. IR (ATR, v/cm⁻¹): v = 3404 (w); 2927 (w); 1646 (s); 1540 (s); 1463 (s); 1382 (m); 1308 (m); 1197 (m); 1142 (m); 804 (m); 735 (m); 655 (w).

 $[Sm(L)(H_2O)(NO_3)(DMF)]$ ·DMF (3). Brown-yellow crystals. Yield: 52%. Anal. Calc. $C_{24}H_{31}N_{10}O_9Sm$ (753.94): C, 38.23; H, 4.14; N, 18.58%. Found: C, 37.44; H, 3.72; N, 18.17%. IR (ATR, v/cm⁻¹): v = 3447 (w); 2929 (w); 1650 (s); 1540 (m); 1467 (m); 1385 (m); 1100 (w); 804 (w); 736 (w); 657 (w).

 $[Eu(L)(H_2O)(NO_3)(DMF)]$ ·DMF (4). Brown-yellow crystals. Yield: 48%. Anal. Calc. $C_{24}H_{31}N_{10}O_9Eu$ (755.55): C, 38.15; H, 4.14; N, 18.54%. Found: C, 37.88; H, 3.78; N, 18.24%. IR (ATR, v/cm⁻¹): v = 3419 (w); 2928 (w); 1649 (s); 1540 (m); 1468 (m); 1384 (m); 1090 (w); 804 (w); 736 (w); 655 (w).

 $[Gd(L)(H_2O)(NO_3)(DMF)]$ ·DMF (5). Brown-yellow crystals. Yield: 58%. Anal. Calc. $C_{24}H_{31}N_{10}O_9Gd$ (760.84): C, 37.89; H, 4.11; N, 18.41%. Found: C, 36.88; H, 3.81; N, 18.22%. IR (ATR, v/cm⁻¹): v = 3420 (w); 2930 (w); 1649 (s); 1541 (m); 1468 (m); 1385 (m); 1102 (w); 804 (w); 735 (w); 656 (w).

 $[Tb(L)(H_2O)(NO_3)(DMF)]$ ·DMF (6). Brown-yellow crystals. Yield: 60%. Anal. Calc. $C_{24}H_{31}N_{10}O_9Tb$ (762.51): C, 37.80; H, 4.10; N, 18.37%. Found: C, 37.40; H, 3.78; N, 18.17%. IR (ATR, v/cm⁻¹): v = 3412 (w); 3221 (w); 2929 (w); 1649 (s); 1541 (m); 1469 (m); 1385 (m); 1104 (w); 805 (w); 736 (w); 656 (w).

 $[Dy(L)(H_2O)(NO_3)(DMF)]$ ·DMF (7). Brown-yellow crystals. Yield: 55%. Anal. Calc. $C_{24}H_{31}N_{10}O_9Dy$ (766.09): C, 37.63; H, 4.08; N, 18.28%. Found: C, 37.68; H, 3.95; N, 18.13%. IR (ATR, v/cm⁻¹): v = 3416 (w); 3215 (w); 2929 (w); 1650 (s); 1543 (m); 1513 (m); 1373 (m); 1306 (w); 1198 (m); 953 (w); 742 (m); 665 (m).

[**Tb**(**L**)(**H**₂**O**)(**NO**₃)(**DMSO**)]·**2H**₂**O** (**6a**). A suspension of **L** (379.4 mg; 1 mmol) in MeOH (30 mL) was heated for 10 min. Then, solid Tb(NO₃)₃·6H₂O (453 mg; 1 mmol) was slowly added to the mixture under continuous heating and stirring to give a yellow solution. After 10 min of heating, Et₃N (1.51 mL; 1.5 mmol) was added dropwise and the mixture was heated for further 15 min. After being cooled to room temperature, yellow powder was collected through suction filtration and washed with methanol. The light-brown needle crystals suitable for X-ray diffraction studies were obtained by recrystallization of a yellow powder from DMSO for over two months at room temperature. Yield: 60%. Elemental Anal. Calc. C₂₀H₂₇N₈O₁₀STb (730.48): C, 32.89; H, 3.73; N, 15.34; S, 4.39%. Found: C, 32.68; H, 3.55; N, 15.13; S, 4.30%. IR (ATR, v/cm⁻¹): v = 3408 (w); 3227 (w); 2918 (w); 1604 (m); 1535 (s); 1469 (s); 1439 (s); 1377 (s); 1305 (m); 1199 (m); 1152 (w); 996 (w); 802 (w); 752 (m).

3. Results and discussion

3.1. IR spectra

The infrared spectra of the all complexes 1-7 were recorded in the region 4000-400 cm⁻¹ (Fig. S1 in ESI). A broad band in the region 3500-3300 cm⁻¹ indicates the presence of water (OH) molecule coordinated to the lanthanide atom [33]. The characteristic C=N stretching of triazine ring in L appears as a medium intensity signal in the region 1550-1480 cm⁻¹ [34]. The IR strong stretching frequency of the C=N is found at 1650-1604 in all the complexes. The positive shift of the v(C=N) band, which is observed at 1618 cm⁻¹ in the free ligand, is related to the coordination of the nitrogen atom of the hydrazine chain group [35]. Weak absorption bands in the region 3200-2900 cm⁻¹ are typical of NH stretching vibrations in hydrazine side chain and a series of absorption bands in the range 1385-1280 cm⁻¹ are typical of the coordinated nitrate group v(N=O)

and $v_{as}(NO_2)$ [36]. The $v_s(NO_2)$ is detected at 1035 cm⁻¹ [37]. After coordination, the various vibrations of Ln-O are assigned to bands occurring at 580-520 cm⁻¹ and Ln-N are assigned to weak bands occurring at 480-410 cm⁻¹, respectively, which confirms the involvement of the oxygen and nitrogen atoms in the coordination sphere of Ln(III) [38]. The series of a weak absorption bands in the range 1270-1150 cm⁻¹ is typical of the C-O-C bonds [39].

Please insert Table 1 here

3.2. Electronic absorption spectra

Solutions of the ligand and complexes for UV-vis absorption and fluorescence measurements were prepared in DMF. The calculations of molar absorption coefficients of the ligand and complexes are summarized in Table 2. Absorption spectrum of the ligand L is characterized by two strong absorption bands with major maxima at 302 nm and 342 nm (Fig. S2 in ESI). Absorption spectra of all the prepared lanthanide complexes are characteristic by disappearance of the second major band observed in the spectrum of the ligand in the 315–360 nm region. A new strong absorption band appears in the 330–450 nm region with major maximum around 372 nm for all the presented complexes. We assume the new absorption band belongs to considerably hyperchromically shifted $n \rightarrow \pi^*$ band of the ligand ($\lambda_{max} = 375$ nm). A similar phenomenon we observed in our previous study dealing with uranium complexes, where the aforementioned absorption band was hyperchromically and slightly hypsochromically shifted [31].

Please insert Figure 1 here

Recorded fluorescence emission spectra of the ligand L and the complexes have one broad relatively uniformly shaped band with one maximum. The emission maximum of the ligand L and complexes 1, 3, 4, 6, 6a and 7 is located in the 422–430 nm region, emission maximum of complex 2 (451 nm) and 5 (460 nm) is bathochromically shifted. All-important luminescence data are summarized in Table 3, emission spectra are presented in Figs. S3-S5 in ESI. Lanthanide-centered emission of the prepared complexes is overlapped by the strong emission signal of the ligand.

Please insert Table 2 here

Please insert Table 3 here

3.3. X-ray structure of complexes

In all the present compounds, lanthanide ions are nine-coordinate. The coordination polyhedron is completed with three nitrogen and two oxygen atoms of the organic chelating ligand, two oxygen atoms of a bidentate nitrate ligand, and two oxygen atoms from water and either DMF (1 to 7) or DMSO (6a) ligands (Fig. 2, 3). The organic ligand inherently forms an equatorial plane which divides the coordination polyhedron in two halves (Fig. 4). While the first is occupied by both the nitrate ligand and the DMF/DMSO, the second one contains a single water ligand. Because of a steric crowd from the former, the equatorial plane of the organic ligand is shifted towards the water ligand. The r.m.s. deviations for the least-squares planes calculated for the five donor atoms of the organic ligand in 1 to 7 range from 0.0667 to 0.0723 Å, and the respective lanthanide ions deviations progressively decrease from 0.5633(9) to 0.5158(8) Å with decreasing ionic radii. The deviation of Tb in 6a (0.5204(8) Å) is in accordance with this trend, although the respective least-squares plane through the donor atoms significantly higher r.m.s. deviation of 0.1898 Å.

Selected bond lengths and angles are listed in Table 5. With decreasing lanthanide radii, the Ln–O and Ln–N bond lengths get progressively shorter in 1 (Pr) to 5 (Gd) and 7 (Dy), which is further reflected in the ligand bite angles. As the smaller lanthanide ions get deeper into the chelate rings, the constituent bite angles get wider while the O2–Ln–O3 angles get narrower.

The water ligands mediate the formation of centrosymmetric dimers *via* two pairs of O—H···O hydrogen bonds to oxygen acceptors from the organic ligands in the other complex molecule (Fig. 5). Another centrosymmetric pairs of N— $H \cdots O$ bonds to oxygen acceptors from the nitrate ligands are responsible for the formation of one-dimensional supramolecular architecture along the b axis. In the isostructural compounds 1 to 6 and 7, donor-acceptor distances are very similar, being on average 2.78 Å for the first of the two O-H···O bonds, 2.67 Å for the second, and 2.87 Å for the N—H…O bond. The related donor-acceptor distances in **6a** are 2.958(2), 2.610(2) and 2.982(2) Å, respectively. A second N-H group from the organic ligand is bound to a solvating DMF molecule in the crystalline complexes 1 to 7. In 6a, two water molecules per formula unit are present, which form a rhomboidal structural unit via hydrogen bonds with their centrosymmetry-related counterparts. These rhomboidal units connect the above-mentioned supramolecular chains through pairs of N-H···O and O-H···N bonds with donor-acceptor distances of 2.816(3) and 2.924(3) Å, respectively. For complexes 1-7, the coordination geometry around the metals were analyzed using by program Shape 2.1 [40]. Any coordination sphere can be described by an ideal polyhedron that has the lowest deviation from the real geometry. The lowest value of deviation for 1-7 was found for spherical capped square antiprism ($C_{4\nu}$) (complete results of the geometric analyses are given in Table 6).

Please insert Figure 2 here

Please insert Figure 3 here

Please insert Figure 4 here

Please insert Figure 5 here

Please insert Table 4 and Table 4 (cont.) here

Please insert Table 5 here

Please insert Table 6 here

3.4. Thermal analyses

TG/DSC experiments show that the complexes **6** and **6a** follow similar decomposition pathways regardless of different solvents present in their structures. The weight losses during heating from 30 to 150 °C correspond to the evaporation of DMF and water for **6** or DMSO and water for **6a**. Degradation of the organic part of the complexes was observed from 300 to 500 °C, and consists of two separated exothermic steps. The total mass losses of 74.9 and 73.9 % for **6** and **6a** (calculated values 75.6 and 74.5, respectively) correspond to the formation of Tb₇O₁₂, which has been confirmed by X-ray powder patterns of final residues left after the TG/DSC experiments (Figs. S6-S7 in ESI).

4. Conclusions

In summary, we have prepared a large, nearly planar *s*-triazine Schiff base ligand by condensation of 2,4-bis(hydrazino)-6-methoxy-1,3,5-triazine with salicylaldehyde and presented its lanthanide complexes, which have been characterized by elemental analysis, IR and UV-vis spectroscopy, thermal analysis, and X-ray diffraction technique. The lanthanide(III) ions are 9-coordinated by six O atoms, two of which come from the nitrate anion, two from the triazine Schiff base ligand, one from water and one from the solvent DMF/DMSO. The ligand behaves as pentadentate with N_3O_2 donor set (two imine nitrogen atoms, one triazine nitrogen atom, and two phenolic group oxygen atoms) and the Ln(III) ions fit the ligand acyclic cavity.

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Appendix A. Supplementary Data

CCDC 1495956-1495963 contain the supplementary crystallographic data for complexes 1-7. 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: <u>deposit@ccdc.cam.ac.uk</u>. Supplementary data associated with this article can be found, in the online version, at

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Figure captions

Scheme 1. Differential reactivity of cyanuric chloride with R-NH₂, R^1 -NH₂, R^2 -NH₂ = N nucleophiles.

Scheme 2. The reaction conditions for preparing L: (a) CH₃OH, NaHCO₃, 10 °C, 1 h; (b) N_2H_4 ·H₂O, THF, reflux 12 h; (c) 2-Hydroxybenzaldehyde, CH₃OH, reflux 24 h.

Fig. 1. The molar absorption coefficients spectra of ligand L, complexes 1-4.

Fig. 2. Molecular structure of 6. Thermal ellipsoids are drawn at the 50% probability level.

Fig. 3. Molecular structure of 6a. Thermal ellipsoids are drawn at the 50% probability level.

Fig. 4. Coordination polyhedron of the europium atom in the complex 4.

Fig. 5. Hydrogen bonding in the crystal structure of **6** and the resulting supramolecular architecture. Solvent DMF and hydrogen atoms were omitted except for (O)H and (N)H.

MA







| Compound | Triazine bands | Selected Type of stretching | v _{O-H} | V _{NO2} (coordinate) | Ln-O (phenolic) | Ln-N |
|----------|----------------|--------------------------------|------------------|----------------------------------|--------------------|------|
| L | 1618 (C=N) | 3118 (N-H) | 3568 | - | - - | - |
| L | 1010 (C=11) | $1573 (C=N_{0.157})$ | 5500 | | | |
| 1 | 1647 (C=N) | 3124 (N-H) | 3417 | 1382; 1308 | 524 | 483 |
| | | 1540 (C=N _{Schiff}) | | | | |
| 2 | 1646 (C=N) | 3116 (N-H) | 3420 | 1379; 1294 | 519 | 478 |
| | | 1540 (C=N _{Schiff}) | | | | |
| 3 | 1650 (C=N) | 3119 (N-H) | 3447 | 1385; 1291 | 520 | 477 |
| | | 1540 (C=N _{Schiff}) | | C | | |
| 4 | 1649 (C=N) | 3120 (N-H) | 3419 | 1384; 1299 | 520 | 477 |
| | | $1540 (C=N_{Schiff})$ | | | | |
| 5 | 1649 (C=N) | 3125 (N-H) | 3420 | 1385; 1301 | 520 | 477 |
| | | 1541 (C=N _{Schiff}) | | | | |
| 6 | 1649 (C=N) | 3125 (N-H) | 3411 | 1385; 1304 | 520 | 477 |
| | | 1541 (C=N _{Schiff}) | | | | |
| 6a | 1629 (C=N) | 3131(N-H) | 3408 | 1378; 1305 | 520 | 477 |
| | | 1535 (C=N _{Schiff}) | | | | |
| | | 1023 (S-O) | | | | |
| 7 | 1650 (C=N) | 3125 (N-H) | 3421 | 1384; 1314 | 520 | 477 |
| | | 1543 (C=N _{Schiff}) | | | | |

Table 1 Selected infrared spectral data of ligand L, and complexes 1-7 (v/cm⁻¹).

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Table 2 Absorption properties of ligand L and complexes 1–7.

| | $\lambda_{\rm max}$, nm, (ε , mol ⁻¹ dm ³ cm ⁻¹) |
|----|--|
| L | 293 (33600), 302 (38800), 332 (36500), 342 (37400), 375 (4900), |
| | 405 (3500) |
| 1 | 295.9 (33700), 308.7 (34200), 372.1 (23300) |
| 2 | 297.4 (29400), 309.2 (33100), 371.6 (24800) |
| 3 | 298.3 (25400), 309.2 (28700), 372.6 (22100) |
| 4 | 298.3 (32000), 309.2 (35400), 371.6 (26900) |
| 5 | 296.9 (29900), 308.8 (30600), 372.2 (23300) |
| 6 | 299.3 (27100), 309.2 (30300), 372.6 (25400) |
| 6a | 295.9 (34900), 307.8 (34400), 372.1 (25500) |
| 7 | 298.3 (25400), 309.2 (23900), 333.0 (8300), 371.6 (22400) |

J³ M, J⁵ M, 6ac = Concentration of $Lc = 1.5 \cdot 10^{-5} \text{ M}$, $1c = 1.9 \cdot 10^{-5} \text{ M}$, $2c = 2.4 \cdot 10^{-5} \text{ M}$, $3c = 2.0 \cdot 10^{-5} \text{ M}$, $4c = 1.8 \cdot 10^{-5} \text{ M}, 5c = 1.9 \cdot 10^{-5} \text{ M}, 6c = 2.0 \cdot 10^{-5} \text{ M}, 6ac = 3.9 \cdot 10^{-5} \text{ M}, 7c = 2.0 \cdot 10^{-5} \text{ M}.$

| $c / \text{mol dm}^{-3}$ | λ_{exc} / nm | $\lambda_{\rm em,\ max}$ / nm |
|--------------------------|---|--|
| $5.5 \cdot 10^{-4}$ | 300 | 429 |
| $9.7 \cdot 10^{-5}$ | 295 | 423 |
| $1.2 \cdot 10^{-4}$ | 308 | 451 |
| $1.0 \cdot 10^{-4}$ | 308 | 422 |
| $9.0 \cdot 10^{-5}$ | 320 | 426 |
| $7.9 \cdot 10^{-5}$ | 308 | 460 |
| $1.5 \cdot 10^{-4}$ | 311 | 430 |
| $1.2 \cdot 10^{-4}$ | 295 | 422 |
| $9.9 \cdot 10^{-5}$ | 311 | 422 |
| | 2 | |
| | $9.7 \cdot 10^{-5} \\ 1.2 \cdot 10^{-4} \\ 1.0 \cdot 10^{-4} \\ 9.0 \cdot 10^{-5} \\ 7.9 \cdot 10^{-5} \\ 1.5 \cdot 10^{-4} \\ 1.2 \cdot 10^{-4} \\ 9.9 \cdot 10^{-5} \\ \end{array}$ | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ |

 Table 3 Luminescence properties data.









Table 4

X-ray structure data collection and refinement parameters for the complexes 1 to 7.

| | 1 | 2 | 3 | 4 |
|---|---------------------------|---------------------------|---------------------------|---------------------------|
| Empirical formula | $C_{24}H_{31}N_{10}O_9Pr$ | $C_{24}H_{31}N_{10}O_9Nd$ | $C_{24}H_{31}N_{10}O_9Sm$ | $C_{24}H_{31}N_{10}O_9Eu$ |
| Formula weight | 744.50 | 747.83 | 753.94 | 755.55 |
| Crystal system | Triclinic | Triclinic | Triclinic | Triclinic |
| Space group | <i>P</i> -1 | <i>P</i> -1 | <i>P</i> -1 | <i>P</i> -1 |
| a (Å) | 10.1082(3) | 10.0858(2) | 10.0616(4) | 10.0649(3) |
| b (Å) | 11.9110(4) | 11.9513(3) | 11.8693(4) | 11.8631(4) |
| c (Å) | 14.0456(4) | 14.0750(3) | 13.9526(5) | 13.9507(4) |
| α (°) | 107.861(3) | 107.901(2) | 107.646(3) | 107.567(3) |
| β (°) | 109.148(3) | 109.105(2) | 108.967(3) | 108.937(2) |
| γ (°) | 97.092(3) | 97.062(2) | 97.021(3) | 97.101(3) |
| $V(Å^3)$ | 1472.55(8) | 1477.62(6) | 1455.91(9) | 1456.04(8) |
| Z | 2 | 2 | 2 | 2 |
| $D_{calcd.}$ (g· cm ⁻³) | 1.679 | 1.681 | 1.720 | 1.723 |
| F(000) | 752 | 754 | 758 | 760 |
| $\mu(\text{mm}^{-1})$ | 1.723 | 1.825 | 1.825 | 2.223 |
| Measured/unique reflections | 18464/5379 | 14312/5403 | 16259/5317 | 14708/5322 |
| Data/restraints/parameters | 5379/2/408 | 5403/2/408 | 5317/2/408 | 5322/2/408 |
| $R_1/wR_2 [I > 2\sigma(I)]$ | 0.0243/0.0533 | 0.0258/0.0762 | 0.0219/0.0507 | 0.0272/0.0587 |
| R_1/wR_2 [all data] | 0.0290/0.0551 | 0.0266/0.0766 | 0.0236/0.0518 | 0.0319/0.0609 |
| GooF | 1.035 | 1.087 | 1.076 | 1.060 |
| $\Delta \rho_{max} / \Delta \rho_{min} (e^{-\dot{A}^{-3}})$ | 0 843/-0 434 | 1 993/-0 682 | 1 139/-0 625 | 1 545/ 0 756 |

Table 4 (cont.)

| Empirical formula C_2 Formula weight76Crystal systemTrSpace group P -a (Å)10b (Å)11c (Å)13 α (°)10 β (°)10 γ (°)97V (ų)14Z2 $D_{calcd.}$ (g· cm⁻³)1.7 | $P_{24}H_{31}N_{10}O_9Gd$ 60.84 riclinic -1 0.0546(2) 1.8642(2) 3.9444(2) 07.472(2) 08.885(2) 7.099(2) 455.66(4) | $C_{24}H_{31}N_{10}O_{9}Tb$ 762.51 Triclinic <i>P</i> -1 10.05090(10) 11.8566(2) 13.9219(2) 107.3600(10) 108.9010(10) 97.0560(10) | C ₂₀ H ₂₇ N ₈ O ₁₀ STb 730.48 Triclinic <i>P</i> -1 9.9332(2) 11.6533(3) 12.0804(3) 107.199(2) 97.010(2) 08.424(2) | $\begin{array}{c} C_{24}H_{31}N_{10}O_{9}Dy\\ 766.09\\ Triclinic\\ P-1\\ 10.04230(10)\\ 11.84790(10)\\ 13.9106(2)\\ 107.2910(10)\\ 108.9070(10)\\ \end{array}$ |
|--|--|---|---|--|
| Formula weight 76 Crystal system Tr Space group P - a (Å) 10 b (Å) 11 c (Å) 13 α (°) 10 β (°) 10 γ (°) 97 V (Å ³) 14 Z 2 $D_{calcd.}$ (g· cm ⁻³) 1.7 | 60.84 riclinic -1 0.0546(2) 1.8642(2) 3.9444(2) 07.472(2) 08.885(2) 7.099(2) 455.66(4) | 762.51 Triclinic <i>P</i> -1 10.05090(10) 11.8566(2) 13.9219(2) 107.3600(10) 108.9010(10) 97.0560(10) | 730.48 Triclinic <i>P</i> -1 9.9332(2) 11.6533(3) 12.0804(3) 107.199(2) 97.010(2) 08.424(2) | 766.09 Triclinic <i>P</i> -1 10.04230(10) 11.84790(10) 13.9106(2) 107.2910(10) 108.9070(10) |
| Crystal system Tr. Space group P - a (Å) 10 b (Å) 11 c (Å) 13 α (°) 10 β (°) 10 γ (°) 97 V (Å ³) 14 Z 2 D _{calcd.} (g· cm ⁻³) 1.7 | riclinic -1 0.0546(2) 1.8642(2) 3.9444(2) 07.472(2) 08.885(2) 7.099(2) 455.66(4) | Triclinic P-1 10.05090(10) 11.8566(2) 13.9219(2) 107.3600(10) 108.9010(10) 97.0560(10) | Triclinic <i>P</i> -1 9.9332(2) 11.6533(3) 12.0804(3) 107.199(2) 97.010(2) 08.424(2) | Triclinic P-1 10.04230(10) 11.84790(10) 13.9106(2) 107.2910(10) 108.9070(10) |
| Space group P - a (Å) 10 b (Å) 11 c (Å) 13 α (°) 10 β (°) 10 γ (°) 97 V (Å ³) 14 Z 2 $D_{calcd.}$ (g· cm ⁻³) 1.7 | -1 0.0546(2) 1.8642(2) 3.9444(2) 07.472(2) 08.885(2) 7.099(2) 455.66(4) | P-1 10.05090(10) 11.8566(2) 13.9219(2) 107.3600(10) 108.9010(10) 97.0560(10) | P-1 9.9332(2) 11.6533(3) 12.0804(3) 107.199(2) 97.010(2) 08.424(2) | P-1 10.04230(10) 11.84790(10) 13.9106(2) 107.2910(10) 108.9070(10) |
| a (Å)10b (Å)11c (Å)13 α (°)10 β (°)10 γ (°)97V (Å3)14Z2 $D_{calcd.}$ (g·cm ⁻³)1.7 | 0.0546(2) 1.8642(2) 3.9444(2) 07.472(2) 08.885(2) 7.099(2) 455.66(4) | 10.05090(10) 11.8566(2) 13.9219(2) 107.3600(10) 108.9010(10) 97.0560(10) | 9.9332(2) 11.6533(3) 12.0804(3) 107.199(2) 97.010(2) 08.424(2) | 10.04230(10) 11.84790(10) 13.9106(2) 107.2910(10) 108.9070(10) |
| b (Å) 11 c (Å) 13 α (°) 10 β (°) 10 γ (°) 97 V (Å ³) 14 Z 2 $D_{calcd.}$ (g·cm ⁻³) 1.7 | 1.8642(2) 3.9444(2) 07.472(2) 08.885(2) 7.099(2) 455.66(4) | 11.8566(2) 13.9219(2) 107.3600(10) 108.9010(10) 97.0560(10) | 11.6533(3) 12.0804(3) 107.199(2) 97.010(2) 08.424(2) | 11.84790(10) 13.9106(2) 107.2910(10) 108.9070(10) |
| c (Å) 13 α (°) 10 β (°) 10 γ (°) 97 V (Å ³) 14 Z 2 D _{calcd.} (g· cm ⁻³) 1.7 | 3.9444(2) 07.472(2) 08.885(2) 7.099(2) 455.66(4) | 13.9219(2) 107.3600(10) 108.9010(10) 97.0560(10) | 12.0804(3) 107.199(2) 97.010(2) 08.424(2) | 13.9106(2) 107.2910(10) 108.9070(10) |
| $\begin{array}{ll} \alpha (^{\circ}) & 10 \\ \beta (^{\circ}) & 10 \\ \gamma (^{\circ}) & 97 \\ V (\mathring{A}^{3}) & 14 \\ Z & 2 \\ D_{calcd.} (g \cdot cm^{-3}) & 1.7 \end{array}$ | 07.472(2) 08.885(2) 7.099(2) 455.66(4) | 107.3600(10) 108.9010(10) 97.0560(10) | 107.199(2) 97.010(2) 08.424(2) | 107.2910(10) 108.9070(10) |
| $\begin{array}{ll} \beta(^{\circ}) & 10 \\ \gamma(^{\circ}) & 97 \\ V(\mathring{A}^{3}) & 14 \\ Z & 2 \\ D_{calcd.}(g\cdotcm^{-3}) & 1.7 \end{array}$ | 08.885(2) 7.099(2) 455.66(4) | 108.9010(10) 97.0560(10) | 97.010(2) | 108.9070(10) |
| γ (°) 97 V (Å ³) 14 Z 2 D _{calcd.} (g· cm ⁻³) 1.7 | 7.099(2) 455.66(4) | 97.0560(10) | 09 424(2) | |
| V (Å ³) 14 Z 2 $D_{calcd.}$ (g·cm ⁻³) 1.7 | 455.66(4) | | 96.424(2) | 97.0400(10) |
| $Z 		 2 		 2 		 D_{calcd.} (g \cdot cm^{-3}) 		 1.7$ | | 1453.18(4) | 1301.03(5) | 1450.47(3) |
| $D_{calcd.} (g \cdot cm^{-3}) \qquad 1.7$ | | 2 | 2 | 2 |
| | .736 | 1.743 | 1.865 | 1.754 |
| F(000) 76 | 62 | 764 | 728 | 766 |
| $\mu(mm^{-1})$ 2.3 | .347 | 2.503 | 2.869 | 2.645 |
| Measured/unique reflections 14 | 4021/5257 | 13968/5285 | 16228/4732 | 13548/5213 |
| Data/restraints/parameters 52 | 257/2/408 | 5285/2/408 | 4732/6/382 | 5213/2/408 |
| $R_1/wR_2 [I > 2\sigma(I)]$ 0.0 | .0149/0.0358 | 0.0158/0.0387 | 0.0181/0.0446 | 0.0167/0.0456 |
| R_1/wR_2 [all data] 0.0 | .0154/0.0359 | 0.0169/0.0418 | 0.0187/0.0449 | 0.0172/0.0497 |
| GooF 1.0 | .077 | 1.135 | 1.068 | 1.180 |
| $\Delta \rho_{\text{max}} / \Delta \rho_{\text{min}}$ (e. Å ⁻³) 0.7 | .715/-0.331 | 0.740/-0.414 | 1.028/-0.527 | 0.763/-0.521 |

Table 5

Selected bond lengths [Å] and angles $[\circ]$ for 1 to 7.

| | 1 | 2 | 3 | 4 | 5 | 6 | 6a | 7 |
|-----------|------------|------------|------------|-----------|------------|------------|------------|------------|
| Ln1–O2 | 2.2988(17) | 2.2937(18) | 2.2659(16) | 2.258(2) | 2.2541(11) | 2.2378(13) | 2.2792(15) | 2.2219(16) |
| Ln1–O3 | 2.3336(17) | 2.3293(18) | 2.3040(16) | 2.301(2) | 2.2954(11) | 2.2843(13) | 2.2158(16) | 2.2754(16) |
| Ln1–O4 | 2.5212(18) | 2.5009(19) | 2.4596(18) | 2.445(2) | 2.4257(11) | 2.4133(14) | 2.4256(16) | 2.3982(16) |
| Ln1–O5 | 2.6410(18) | 2.6270(19) | 2.5996(17) | 2.583(2) | 2.5779(11) | 2.5697(14) | 2.5985(17) | 2.5588(17) |
| Ln1–O6 | 2.6430(17) | 2.6351(19) | 2.6083(17) | 2.595(2) | 2.5895(11) | 2.5805(14) | 2.5349(16) | 2.5703(16) |
| Ln1–O8 | 2.5073(19) | 2.489(2) | 2.4621(18) | 2.454(2) | 2.4372(12) | 2.4262(14) | 2.4176(16) | 2.4115(17) |
| Ln1–N3 | 2.550(2) | 2.534(2) | 2.5046(19) | 2.491(3) | 2.4849(13) | 2.4709(16) | 2.4518(18) | 2.4581(19) |
| Ln1–N6 | 2.678(2) | 2.664(2) | 2.632(2) | 2.623(2) | 2.6135(14) | 2.6056(16) | 2.5689(19) | 2.5954(19) |
| Ln1–N7 | 2.664(2) | 2.654(2) | 2.6254(19) | 2.616(2) | 2.6082(13) | 2.5956(16) | 2.5899(18) | 2.5857(19) |
| O2-Ln1-O3 | 89.55(6) | 88.78(6) | 87.49(6) | 86.93(8) | 86.24(4) | 85.50(5) | 85.07(6) | 85.17(6) |
| O2-Ln1-N6 | 68.28(6) | 68.41(7) | 69.02(6) | 69.11(8) | 69.38(4) | 69.60(5) | 69.34(6) | 69.72(6) |
| O3–Ln1–N7 | 67.90(6) | 68.17(7) | 68.41(6) | 68.67(8) | 68.73(4) | 68.97(5) | 70.81(6) | 69.00(6) |
| N3-Ln1-N6 | 61.70(6) | 62.01(7) | 62.50(6) | 62.74(8) | 62.85(4) | 63.10(5) | 63.62(6) | 63.26(6) |
| N3-Ln1-N7 | 61.78(6) | 62.04(7) | 62.58(6) | 62.68(7) | 62.97(4) | 63.23(5) | 63.28(6) | 63.43(6) |
| N6-Ln1-N7 | 121.85(6) | 122.40(7) | 123.46(6) | 123.81(8) | 124.16(4) | 124.68(5) | 124.90(6) | 125.01(6) |
| | | | | | | | | |

Table 6

Results of continuous shape measures calculations using program SHAPE 2.1 for complexes 1-7.^a

| | Pr ¹ (III) | Nd ² (III) | Sm ³ (III) | Eu ⁴ (III) | Gd ⁵ (III) | Tb ⁶ (III) | Tb ^{6a} (III) | Dy ⁷ (III) |
|-------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|------------------------|-----------------------|
| CN=9 ^b | | | | | | | | |
| CCU-9 | 7.927 | 7.893 | 7.954 | 7.950 | 8.010 | 8.080 | 6.854 | 8.083 |
| JCSAPR-9 | 2.508 | 2.441 | 2.393 | 2.362 | 2.328 | 2.308 | 2.080 | 2.266 |
| CSAPR-9 | 1.831 | 1.763 | 1.697 | 1.670 | 1.632 | 1.613 | 1.383 | 1.575 |
| JTCTPR-9 | 4.079 | 4.079 | 3.991 | 3.974 | 3.954 | 3.960 | 3.276 | 3.932 |
| JCCU-9 | 8.912 | 8.885 | 8.958 | 8.952 | 9.014 | 9.080 | 7.905 | 9.079 |

^a The listed values correspond to the deviation between the ideal and real coordination polyhedra, the lowest values are in red color.

^bCCU-9 = spherical capped cube, JCSAPR-9 = capped square antiprism J10, CSAPR-9 = spherical capped square antiprism, JTCTPR-9 = tricapped trigonal prism J51, JCCU-9 = capped cube J8.

Graphical abstract



- Eight new lanthanide(III) complexes of a Schiff-base ligands based on *s*-triazine derivative have been synthesized.
- The X-ray crystal structures of $[Pr(L)(H_2O)(NO_3)(DMF)] \cdot DMF$ (1), [Nd(L)(H₂O)(NO₃)(DMF)]·DMF (2), [Sm(L)(H₂O)(NO₃)(DMF)]·DMF (3), [Eu(L)(H₂O)(NO₃)(DMF)]·DMF (4), $[Gd(L)(H_2O)(NO_3)(DMF)] \cdot DMF$ (5), $[Tb(L)(H_2O)(NO_3)(DMF)] \cdot DMF$ (6), $[Tb(L)(H_2O)(NO_3)(DMSO)] \cdot 2H_2O$ (**6a**), $[Dy(L)(H_2O)(NO_3)(DMF)]$ ·DMF (7) have been determined.
- The luminescence, FTIR and UV-vis spectra of all complexes 1-7 have been studied.
- The TG and +DSC analyses of all complexes 1-7 have been determined.