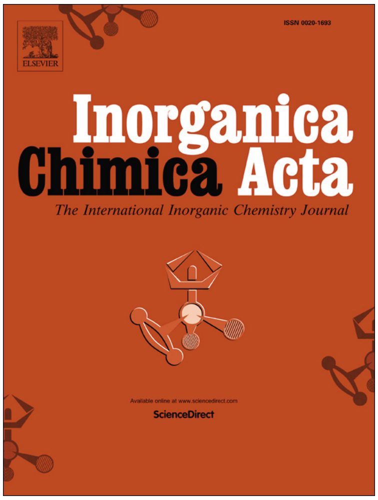

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One-pot metal template synthesis, crystal structures and spectroscopic properties of self-assembled rare earth metal ion complexes of salicylaldimine ligands

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Abstract

The one-step metal-promoted condensation reaction of salicylaldehyde with diethylenetriamine in the presence of rare earth metal ions carried out in the same experimental conditions produces two types of salicylaldimine complexes. The compounds were characterized by spectroscopic data (ESI-MS, IR, UV/Vis, luminescence) and X-ray crystallography. The complexes contain the deprotonated tetradentate $C_{11}H_{16}N_3O=(L^1)^{1-}$ *N*-(salicylidene)-diethylenetriamine or pentadentate $C_{18}H_{19}N_3O_2=(L^2)^{2-}$ *N,N'*-bis(salicylidene)-diethylenetriamine ligand as a result of the [1+1] or [2+1] Schiff base condensation, respectively. The metal ions are bonded to all the potential nitrogen and oxygen donor atoms. The crystal structures of the complexes reveal two different supramolecular architectures: a monomer in $[Tm(C_{11}H_{16}N_3O)_2]NO_3\cdot CH_3OH$ complex with formation of a two-dimensional self-assembled network and a dimer in $[M_2(C_{18}H_{19}N_3O_2)_2(NO_3)_2]$ complexes (M = Y^{3+}, Eu^{3+}or Lu^{3+}), although in all cases the metal ions are eight-coordinated with distorted square antiprism geometry.

Keywords: Rare earth metal ions; Self-assembly; Schiff base complexes; Crystal structures

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1. Introduction

Metal complexes of Schiff base salen-type chelating ligands with N and O potential donor atoms are called metallo-salens. They are stable in solution and in the solid state [1]. The salen-type ligands can coordinate to various d- and f-block metal cations. The rare earth metal ion (yttrium and lanthanides) Schiff base complexes are of special interest due to their potential use in organic light-emitting diodes, as luminescent molecular probes, as a new generation of functional materials, in catalysis, as single-molecule magnets (SMM) [2-8], in biological applications [9-11]. Many supramolecular structures of salen-type rare earth metal ion complexes are known, sometimes with unexpected and unusual coordination framework [2,3,12-21]. This may be due to the difficulties in controlling the coordination environment around these metal ions which display high and variable coordination numbers with low stereochemical preference. Recently we reported the metal promoted in situ synthesis and the structural details of salicylaldimine lanthanide nitrate complexes derived from salicylaldehyde and flexible aliphatic or rigid aromatic diamines which self-assemble into an infinite one- or two-dimensional coordination polymers, finite monomers and dimers with an unusual coordination mode [17-19]. The salen-type ligands with N_2O_2 set of potential donor atoms exist in these complexes in neutral form and use exclusively the oxygen atoms as donors with the nitrogen atoms not being involved in the coordination [17-21]. In order to extend our study on influence of the nature of diamine spacer on supramolecular array, we used diethylenetriamine as precursor with additional nitrogen atom as potential donor. Here we describe the template synthesis, single crystal X-ray structure determination and characterization of rare earth metal ion salicylaldimine complexes containing tetradentate *N*-(salicylidene)-diethylenetriamine with N_3O set of donor atoms or pentadentate *N,N'*-bis(salicylidene)-diethylenetriamine ligand with N_3O_2 donor system. Two types of the complexes have been isolated as a result of a self-organization process starting from Schiff base [1+1] or [2+1] condensation of salicylaldehyde and diamine in the presence of rare earth metal ions (Scheme S1, Supplementary material). Contrary to our earlier findings the metal ions in these complexes are bonded to all the potential nitrogen and oxygen donor atoms of the deprotonated ligands.

2. Experimental

2.1. Materials

$Y(NO_3)_3{\cdot}6H_2O$, $Eu(NO_3)_3{\cdot}5H_2O$, $Tm(NO_3)_3{\cdot}6H_2O$, $Lu(NO_3)_3{\cdot}6H_2O$, salicylaldehyde and diethylenetriamine were used as received from Aldrich Chemical Company.

2.2. Physical measurements

The compounds were characterized using microanalyses (CHN), IR, ESI-MS, and single crystal X-ray structural analysis.

IR spectra were recorded using KBr pellets in the range of 4000-400 cm^{-1} on a Bruker IFS 66v/S spectrophotometer. Mass spectra were recorded using electrospray ionization (ESI) techniques. Electrospray mass spectra were determined in methanol using a Waters Micromass ZQ spectrometer. Microanalyses (CHN) was obtained using a Perkin-Elmer 2400 CHN micro analyzer. Ultraviolet–visible (UV–Vis) spectra of the compounds in ethanol (at concentration of $2{\cdot}10^{-5}$ M) were measured using Shimadzu UV PC 2401 spectrophotometer. Luminescence spectra (scanned from 200 to 660 nm) were recorded on a Hitachi F 7000 spectrofluorometer with a 1 cm quartz cell at room temperature. Both of the excitation and emission band widths were 2.5 nm.

2.3. Synthesis of the complexes. General procedures.

$[Tm(C_{11}H_{16}N_3O)_2]NO_3\cdot CH_3OH$; $[M_2(C_{18}H_{19}N_3O_2)_2(NO_3)_2]$ ($M=Y^{3+}$, Eu^{3+}, Lu^{3+})

To a mixture of appropriate metal(III) nitrate (0.1 mmol: 46 mg $Tm(NO_3)_3\cdot 6H_2O$ for **1**, 38 mg $Y(NO_3)_3\cdot 6H_2O$ for **2**, 43 mg $Eu(NO_3)_3\cdot 5H_2O$ for **3**, 47 mg $Lu(NO_3)_3\cdot 6H_2O$ for **4**) in methanol (10 mL) and salicylaldehyde (0.2 mmol, 16 μL) in methanol (5 mL), diethylenetriamine (0.1 mmol, 11 μL) in methanol (5 mL) was added dropwise (30 min) with stirring. The reaction was carried out under air for 48 hours at room temperature, which resulted in formation of clear yellow solution. The solution volume was then reduced to 5 mL by roto-evaporation. Dark-yellow single crystals suitable for X-ray diffraction analysis were formed by slow diffusion of dichloromethane or *n*-hexane (1a) into reaction sample at 4°C over a period of 6-8 weeks. Single crystals were filtered via suction filtration and air dried.

$[Tm(C_{11}H_{16}N_3O)_2]NO_3\cdot CH_3OH$ (*1*)

Yield: 43mg, 0.063 mmol, 63%. *Anal.*: Calcd. for $C_{23}H_{36}N_7O_6Tm$ (675.52 g mol^{-1}): C, 40.89; H, 5.37; N, 14.51. Found: C, 42.08; H, 4.99; N, 14.71%. ESI-MS: *m/z* = 580 $[Tm(C_{11}H_{16}N_3O)_2]^+$, 205 $[C_{11}H_{16}N_3O]^-$. IR (KBr): ν = 3435 (OH), 3322, 3281, 3230 (NH), 2425 (OH⊙⊙⊙N), 1631 (C=N), 1608 (C=C), 1763, 1474, 1384, 1347, 825 (NO_3^-), 1257 (C–O), 570 (Tm–N), 485 (Tm–O) cm^{-1}. UV-Vis (EtOH): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 254 ($1.55\cdot 10^4$), 325 ($0.52\cdot 10^4$).

$[Y_2(C_{18}H_{19}N_3O_2)_2(NO_3)_2]$ (*2*)

Yield: 60 mg, 0.065 mmol, 66%. *Anal.*: Calcd. for $C_{36}H_{38}N_8O_{10}Y_2$ (920.56 g mol^{-1}): C, 46.97; H, 4.16; N, 12.17. Found C, 46.91; H, 4.19; N, 12.13%. ESI-MS: *m/z* = 709 $[Y(C_{18}H_{20}N_3O_2)_2]^+$, 398 $[Y(C_{18}H_{19}N_3O_2)]^+$, 522 $[Y(C_{18}H_{20}N_3O_2)_2(NO_3)_2]^-$, 312 $[C_{18}H_{21}N_3O_2+H]^+$. IR (KBr): ν = 3418 (OH), 3272, 3070, 3014 (NH), 1635 (C=N), 1597

(C=C), 1779, 1742, 1483–1326, 826, 817 (NO_3^-), 1273 (C–O), 556 (Y–N), 480 (Y–O) cm^{-1}. UV-Vis (EtOH): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 258 ($3.09 \cdot 10^4$), 346 ($1.58 \cdot 10^4$).

$[Eu_2(C_{18}H_{19}N_3O_2)_2(NO_3)_2]$ ***(3)***

Yield: 65 mg, 0.062 mmol, 62%. *Anal.*: Calcd. for $C_{36}H_{38}N_8O_{10}Eu_2$ (1044.66 g mol^{-1}): C, 41.31; H, 3.66; N, 10.71. Found C, 41.53; H, 3.61; N, 10.68%. ESI-MS: *m/z* = 773 $[Eu(C_{18}H_{20}N_3O_2)_2]^+$, 586 $[Eu(C_{18}H_{20}N_3O_2)_2(NO_3)_2]^-$, 312 $[C_{18}H_{21}N_3O_2+H]^+$. IR (KBr): ν = 3428 (OH), 3258, 3151, 3037 (NH), 1633 (C=N), 1595 (C=C), 1767, 1738, 1472–1303, 830, 819 (NO_3^-), 1273 (C–O), 560 (Eu–N), 483 (Eu–O) cm^{-1}. UV-Vis (EtOH): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 261 ($2.63 \cdot 10^4$), 348 ($1.66 \cdot 10^4$).

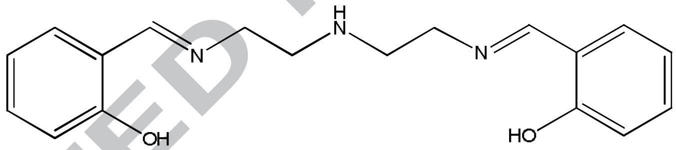
$[Lu_2(C_{18}H_{19}N_3O_2)_2(NO_3)_2]$ ***(4)***

Yield: 71 mg, 0.065 mmol, 65%. *Anal.*: Calcd. for $C_{36}H_{38}N_8O_{10}Lu_2$ (1092.68 g mol^{-1}): C, 39.57; H, 3.51; N, 10.26. Found C, 39.61; H, 3.59; N, 10.29%. ESI-MS: *m/z* = 795 $[Lu(C_{18}H_{20}N_3O_2)_2]^+$, 312 $[C_{18}H_{21}N_3O_2+H]^+$. IR (KBr): ν = 3424 (OH), 3257, 3162, 3042 (NH), 1631 (C=N), 1596 (C=C), 1767, 1753, 1471–1326, 827, 818 (NO_3^-), 1276 (C–O), 572 (Lu–N), 488 (Lu–O) cm^{-1}. UV-Vis (EtOH): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 259 ($2.19 \cdot 10^4$), 347 ($1.05 \cdot 10^4$).

2.4. Synthesis of the N,N'-bis(salicylidene)-diethylenetriamine, $H_2L^2=C_{18}H_{21}N_3O_2$

The *N,N'*-bis(salicylidene)-diethylenetriamine (H_2L^2) has been obtained for comparison by Schiff base [2+1] condensation reaction of salicylaldehyde and diethylenetriamine using method described earlier for *N,N'*-bis(salicylidene)-ethylenediamine with some modifications [22]. To a solution of salicylaldehyde (320 μL, 4 mmol) in a mixed solvent of toluene (15 mL) and diethyl ether (5 mL), diethylenetriamine (220 μL, 2 mmol) in THF (15 mL) was added dropwise with stirring. The reaction was carried out for 3 h at 50°C. The yellow solution was acidified with glacial acetic acid to pH 6 and after 0.5 h the mixture was cooled. The solution volume was then reduced to 5 mL by roto-evaporation. Precipitation was carried out by addition of diethyl ether (5 mL). The yellow solid was filtered off and dried in air.

Yield: 252 mg, 0.809 mmol, 81%. *Anal.*: Calcd. for $C_{18}H_{21}N_3O_2$ (311.38 g mol^{-1}): C, 69.43; H, 6.80; N, 13.49. Found C, 69.11; H, 6.65; N, 13.19%. ESI-MS: *m/z* = 310 $[C_{18}H_{21}N_3O_2\text{-}H]^-$, 312 $[C_{18}H_{21}N_3O_2\text{+}H]^+$. IR (KBr): ν = 3389 (OH), 2575 (OH···N), 1628 (C=N), 1582 (C=C), 1281 (C–O) cm^{-1}. UV-Vis (EtOH): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 255 ($0.44 \cdot 10^4$), 313 ($0.16 \cdot 10^4$), 402 ($0.05 \cdot 10^4$).



Scheme 1. Schiff base ligand H_2L^2

2.5. X-ray crystallography

Diffraction data were collected by the ω-scan technique on Agilent Technologies four-circle SuperNova diffractometer with Atlas CCD detector, equipped with Nova microfocus CuK_α radiation source (λ = 1.54178 Å), for **2** and **3** at room temperature, for **1**, **1a** and **4** at 130(1) K. The data were corrected for Lorentz-polarization as well as for absorption effects [23]. Precise unit-cell parameters were determined by a least-squares fit of reflections of the highest intensity, chosen from the whole experiments. The structures were solved with SIR92

[24] and refined with the full-matrix least-squares procedure on F^2 by SHELXL-2013 [25]. The scattering factors incorporated in SHELXL97 were used. All non-hydrogen atoms were refined anisotropically, N-H hydrogen atoms in **1** were found in difference Fourier maps and isotropically refined, all other hydrogen atoms were placed in idealized positions and refined as 'riding model' with isotropic displacement parameters set at 1.2 times U_{eq} of appropriate carrier atoms. In the structures of **2** and **4** the large voids were filled with diffused electron density; as the modeling of solvent molecules was in these cases unsuccessful, the SQUEEZE procedure [26] was applied. Crystals of **3** were found to be two-component twins and this was taken into account both in data reduction and structure refinement. These crystals were of poor quality, and the diffraction finished quickly – therefore the data found up to 1.1Å resolution were only collected. As this structure is isostructural with previously reported for Nd^{3+} complex [27] we will not discuss it in detail (Crystal data for **1**-**4** complexes, Supplementary material).

3. Results and discussion

3.1. Synthesis, ESI mass and IR spectroscopy

The salen-type rare earth metal ion complexes containing either *N*-(salicylidene)-diethylenetriamine for Tm^{3+} (**1**) or *N,N'*-bis(salicylidene)-1,5-diethylenetriamine for Y^{3+} (**2**), Eu^{3+} (**3**) or Lu^{3+} (**4**) were prepared in situ through the one-step Schiff base condensation reaction of salicylaldehyde with diethylenetriamine in the presence of appropriate nitrate salt acting as a template. It should be noted here that, although these complexes were synthesized by the template procedure, the free *N,N'*-bis(salicylidene)-diethylenetriamine ligand was also obtained separately for comparison.

The complexes were characterized by ESI mass spectroscopy and IR spectral analysis. The mass spectra of complexes showed mass fragmentation pattern which fits well with the formula suggested by elemental and X-ray analyses. The ESI mass spectra exhibit mass peak corresponding to the free ligand as a result of demetalation process. The mass spectrum of ligand H_2L^2 showed molecular ion peaks at $m/z = 310$ $[C_{18}H_{21}N_3O_2\text{-H}]^-$, 312 $[C_{18}H_{21}N_3O_2\text{+H}]^+$ which matched the $C_{18}H_{21}N_3O_2$ ligand formula. The infrared spectra of the complexes provide some information regarding the bonding mode of the ligand and nitrate counterions. All IR spectra of complexes exhibit three bands at 3322-3014 cm^{-1} region attributable to NH vibrations of amine groups. The IR spectrum of ligand H_2L^2 exhibits the bands at 3389 cm^{-1} and 2557 cm^{-1} characteristic of O-H stretching vibration and OH···N=C moiety, respectively. The presence of these bands in the ligand indicates that hydrogen atom of the phenol is involved in intramolecular H-bonding with the imine nitrogen. The IR spectrum of Tm^{3+} complex **1** displays a band at 3435 cm^{-1} corresponding to OH vibration in the MeOH molecules. The band at 2425 cm^{-1} is attributed to the presence of intermolecular hydrogen bonds between NH groups and nitrate oxygen atoms, involving also solvent molecules which is consistent with crystallographic data. All IR spectra of compounds exhibit characteristic absorption band at around 1630 cm^{-1} attributed to C=N stretching mode confirming the Schiff base formation. The shift of this band to higher frequency, observed in the spectra of the complexes compared to the free ligand confirms the coordination of the nitrogen atom of azomethine group to the rare earth ions. The spectrum of complex **1** exhibits two strong bands at 1384 and 825 cm^{-1}, suggesting the ionic nature of nitrate anion The spectra of the complexes **2**, **3** and **4** display vibrations indicative of coordinated nitrate groups. The ν(N–O) stretching frequencies are observed at 1488-1303 cm^{-1} region. The range of splitting confirms the bidentate coordinating behavior of the nitrate groups [28]. The ν(C–O) phenolic frequency observed as a band at 1281 cm^{-1} for the ligand H_2L^2, is shifted in the complexes thus suggesting the participation of the oxygen atom of the deprotonated hydroxyl group in the formation of the M–O bonds. The metal complexes are also characterized by appearance of new bands at 572-556 cm^{-1} and 488-480 cm^{-1} which are assigned to ν(M–N) and ν(M–O) bending frequencies, respectively.

3.2. Crystal structure

The complex $[Tm(L^1)_2]^+\cdot NO_3^-$ has been obtained in two different crystal forms: orthorhombic Pbca **1** and monoclinic $P2_1/n$ **1a**, the latter ones crystallizes with two structural units (Table 1a **A**, **B**) in the asymmetric part of the unit cell. Interestingly, in both of these crystals there are additional solvent (methanol) molecules (one per asymmetric unit in **1**, two in **1a**). The crystals **1** and **1a** were obtained from the same synthesis, but were crystallized in two different vials. The crystals **1** and **1a** were of irregular form and differed from each other in shade and shape (Fig. S1, Supplementary material). The geometric features of the complexes are almost identical; Tm^{3+} cations are eight-coordinated by one oxygen and three nitrogen atoms from two ligand molecules (Fig. 1), the nitrate counteranions are not involved in coordination.

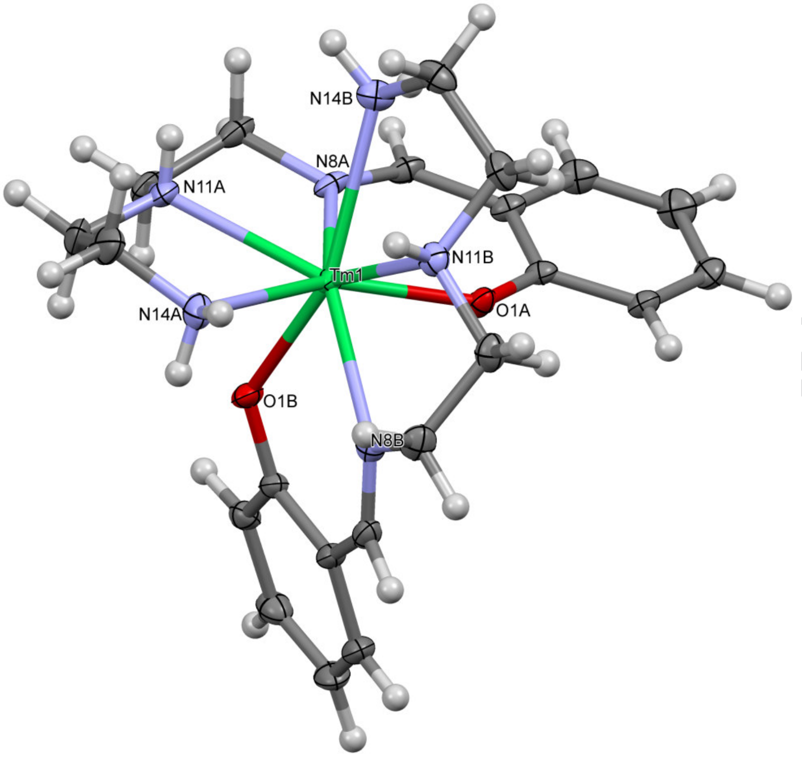


Fig. 1. A perspective view of the $[Tm(L^1)_2]^+$ cation in **1**; ellipsoids are drawn at the 50% probability level, hydrogen atoms are shown as spheres of arbitrary radius.

The coordination geometry in each case can be described as distorted square antiprism: N11 and N14 atoms from two ligand molecules are approximately coplanar, and the mean plane is almost parallel to the plane created by O1 and N8 atoms. Also the Tm-ligand bond lengths are similar in two molecules. Table 1a lists relevant geometrical data for the complexes. In the crystal structures hydrogen bond networks between NH groups and nitro oxygen atoms, involving also solvent molecules, are influencing the architecture of the crystals (Fig. 2, Table S1, Supplementary material).

Table 1

Geometrical parameters (Å); (a) – type 1, (b) – type 2.

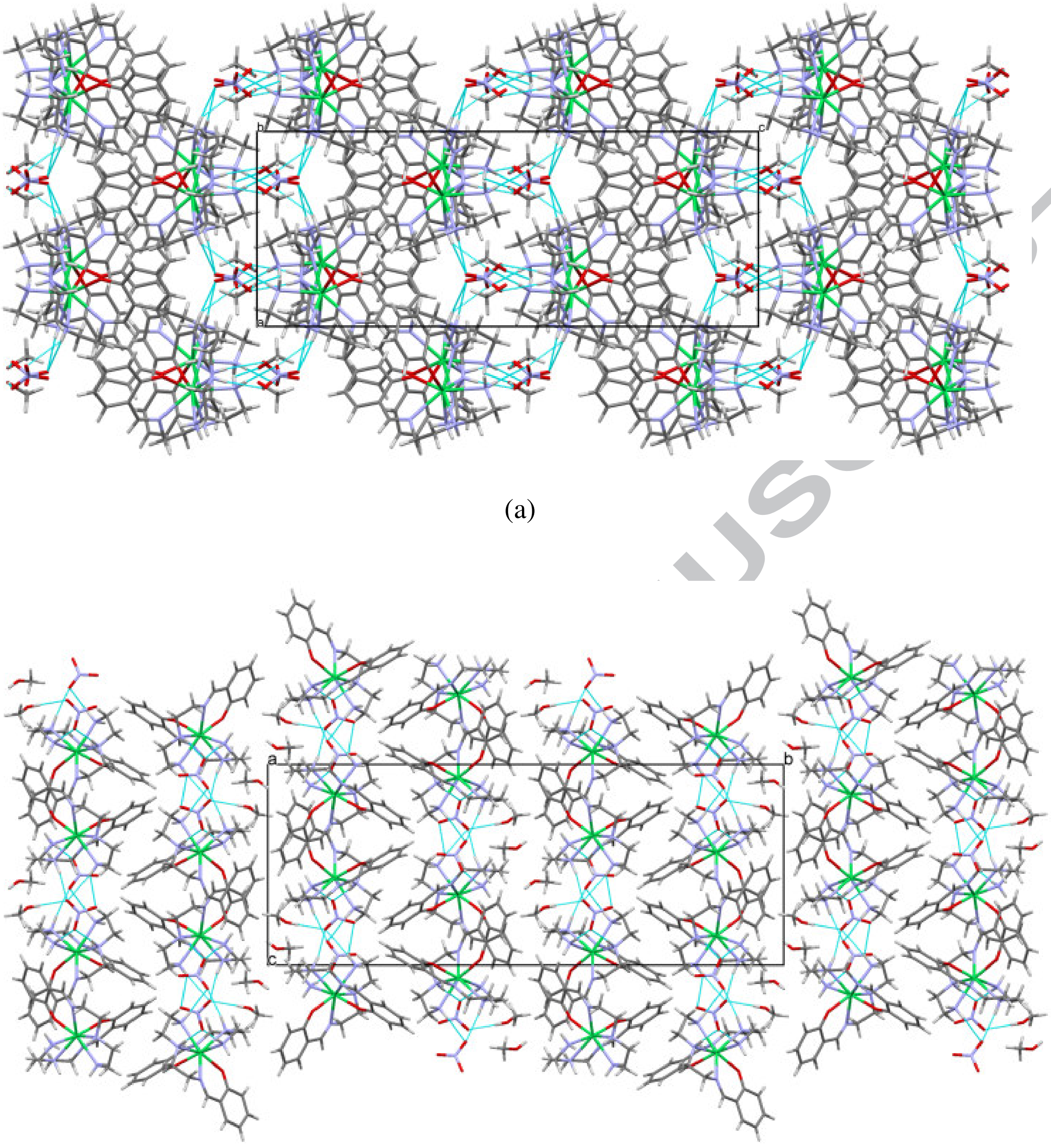
(a)

	1 (M=Tm)	**1a (M=Tm)**	
		A	**B**
M-O1A	2.177(2)	2.171(5)	2.173(5)
M-O1B	2.172(2)	2.155(5)	2.150(6)
M-N8A	2.503(3)	2.468(7)	2.501(7)
M-N8B	2.482(3)	2.487(6)	2.521(6)
M-N11A	2.504(3)	2.521(6)	2.509(7)
M-N11B	2.512(3)	2.511(6)	2.502(7)
M-N14A	2.538(3)	2.511(7	2.521(7)
M-N14B	2.555(3)	2.514(6)	2.527(7)

(b)

	2 (M=Y)	**3 (M=Lu)**	**4 (M=Eu)**
M-O1A	2.1716(16)	2.157(3)	2.28(4)
M-O17A	2.3131(14)	2.279(3)	2.36(3)
M-O17A	2.2891(14) $^{\mathrm{i}}$	2.243(3) $^{\mathrm{ii}}$	2.36(3) $^{\mathrm{iii}}$
M-O2B	2.4913(16)	2.408(3)	2.51(4)
M-O3B	2.4548(16)	2.463(3)	2.52(3)
M-N8A	2.4961(19)	2.455(4)	2.56(4)
M-N11A	2.5280(18)	2.488(4)	2.60(4)
M-N14A	2.5408(19)	2.494(4)	2.54(4)
M···M	3.7283(4) $^{\mathrm{i}}$	3.6680(4) $^{\mathrm{ii}}$	3.835(6) $^{\mathrm{iii}}$

Symmetry codes: $^{\mathrm{i}}$ *1/2-x,1/2-y,-z,* $^{\mathrm{ii}}$ *½-x,1/2-y,1-z*; $^{\mathrm{iii}}$ *–x,2-y,-z*



(a)

(b)

Fig. 2. 2-D layer structure in **1** constructed by hydrogen bonding as seen along *x* (a) and *z* (b) directions.

For the second type of complexes, with $(L^2)^{2-}$ ligand, we have found two different crystal structures, both created by the neutral dimeric units, which can be described as $M_2(L^2)_2(NO_3)_2$

(M=Y^{3+}, Eu^{3+}or Lu^{3+}). Relevant geometrical data are presented in Table 1b. One of these forms – monoclinic $P2_1$ – was described earlier for Nd complex [27], and now we obtained isomorphic structure for Eu^{3+} (**3**) prepared in completely different in situ method. Complexes of Y^{3+} (**2**) and Lu^{3+} (**4**) crystallize in yet another form, C2/c monoclinic. Again, the geometry of the complexes is almost identical in these crystals (Fig. 3); they are binuclear di-O bridged, centrosymmetric dimers. In both forms the crystals are exactly C_i-symmetrical, as they occupy special positions in their respective space groups. The rare earth metal ions are 8-coordinated, this time by one N_3O_2 system from $(L^2)^2$ ligand molecule, bridging oxygen from another $(L^2)^{2-}$ and two oxygen atoms from the nitrate anion, and the coordination geometry is distorted square antiprism. Fig. S2 (Supplementary material) shows the crystal structure of $[Y_2(C_{18}H_{19}N_3O_2)_2(NO_3)_2]$ **2**; the large gaps which are filled with the diffused electron density (disordered solvents, for instance) are clearly seen.

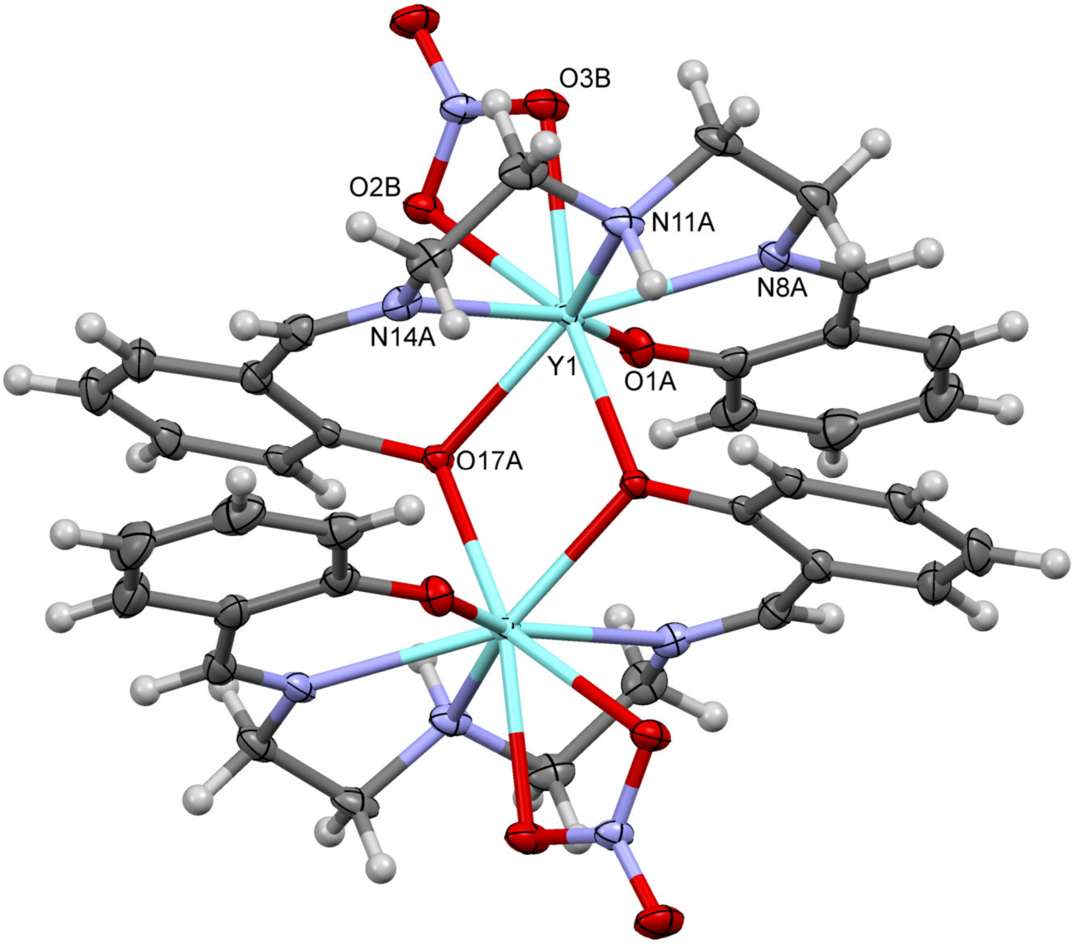


Fig. 3. A perspective view of the $[Y_2(L^2)_2(NO_3)_2]$ centrosymmetric complex in **2**; ellipsoids are drawn at the 50% probability level, hydrogen atoms are shown as spheres of arbitrary radius. The unlabeled atoms are related to the labelled ones with symmetry operation *-x+1/2, -y+1/2, -z.*

3.3. Electronic absorption spectra and luminescence properties

Absorption and emission spectra of ligand H_2L^2 and complexes **1**-**4** were recorded at concentration of $2{\cdot}10^{-5}$ M in ethanol solvent at ambient temperature. The absorption maxima bands (λ_{max}) and the molar absorption coefficients (ε) are listed in Table 2 and selected spectra are presented in Fig. 4.

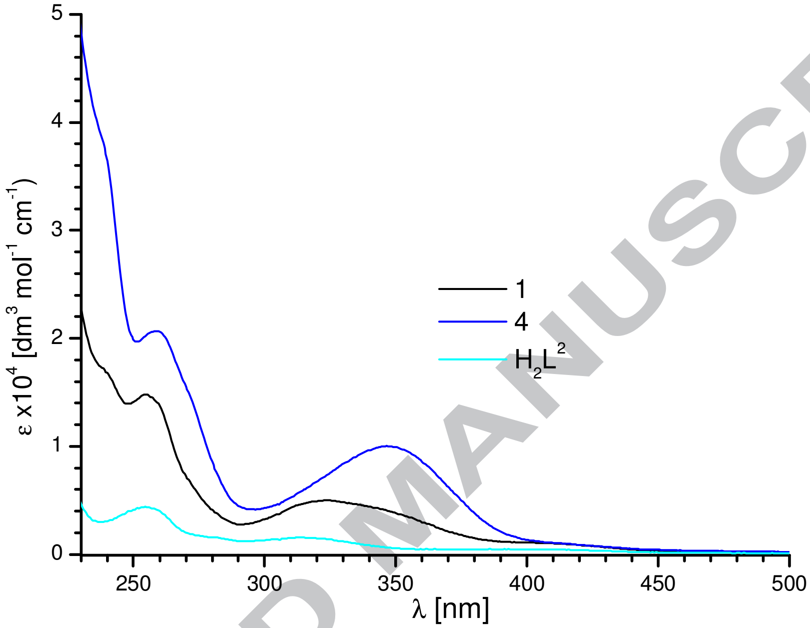


Fig. 4. The UV-Vis absorption spectra of the ligand H_2L^2 and complexes **1** and **4** in ethanol solution.

The absorption of ligand H_2L^2 is characterized by two main bands at λ_{max}=255 and 313 nm. These absorption bands are ascribable to π-π* transitions involving both the benzene ring and azomethine group [29,30]. Upon complexation, in **2**-**4** these bands are red-shifted to 258-261 and 346-348 nm compared to those of free ligand. The very low intensity absorption band at λ=402 nm observed in H_2L^2 may belong the n-π* transition of the C=N group which overlaps with intramolecular charge transfer from phenyl ring. In the case of complex **1** with $(L^1)^{1-}$, the main absorption bands are located at 254 and 325 nm. The f-f transitions of the lanthanide(III) ions are very weak and were not observed in the absorption spectra of the complexes.

Table 2

Electronic spectral data of ligand H_2L^2 and complexes **1**-**4**.

Compound	Absorption λ_{abs}/nm ($\varepsilon \cdot 10^4$/$dm^3 \cdot mol^{-1} \cdot cm^{-1}$)	Excitation λ_{ex}/nm	Emission λ_{em}/nm
H_2L^2	255 (0.44), 313 (0.16), 402 (0.05)	360	433
1	254 (1.55), 325 (0.52)	362	437
2	258 (3.09), 346 (1.58)	348	442
3	261 (2.63), 348 (1.66)	361	440
4	259 (2.19), 347 (1.05)	353	435

The photoluminescent properties of all the complexes along with the H_2L^2 ligand were also studied. The excitation wavelengths were selected from excitation spectra of the complexes. Upon excitation at 360 nm, a blue emission with broad spectral profile centered at about 433 nm was observed for Schiff base ligand. The luminescence spectra of **1-4** complexes, shown in Fig. 5, only exhibited free ligand emission bands centered at 437, 442, 440 and 435 nm respectively. The luminescence of these compounds is most likely caused by π-π* or n-π* intra-ligand transitions [31,32]. The intramolecular energy transfer from the ligand triplet state to excited states of lanthanide(III) ions is one of the factors influencing the luminescence properties of lanthanide(III) complexes [33]. The spectrum of the Eu^{3+} complex **3** does not exhibit bands characteristic of metal-centered emission. The absence of emission bands of Eu^{3+} ions may be due to the quenching through an intra-ligand and ligand-to-europium charge-transfer excited states [34].

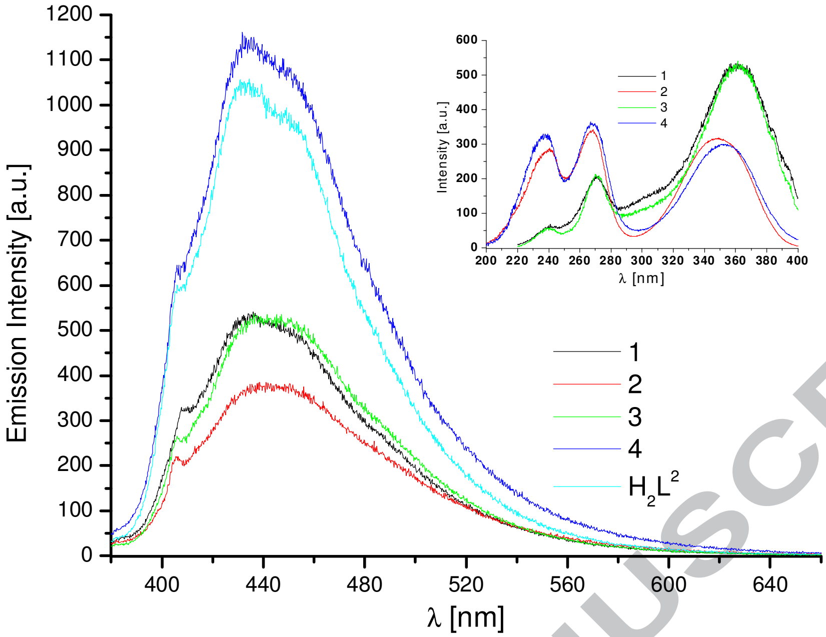


Fig. 5. Emission and excitation spectra of studied compounds in ethanol solution.

4. Conclusion

The rare earth nitrate complexes of *N*-(salicylidene)-diethylenetriamine or *N,N'*-bis(salicylidene)-1,5-diethylenetriamine are formed in situ through the self-assembly process in the metal-induced [1+1] or [2+1] Schiff base condensation reaction of salicylaldehyde with diethylenetriamine. Crystal structure determination reveals the formation of the monomer in case of thulium(III) *N*-(salicylidene)-diethylenetriamine complex with 1:2 metal to ligand stoichiometry, where the Schiff base acts as deprotonated tetradentate ligand with N_3O set of donor atoms. The hydrogen bonding leads to formation of a 2-D self-assembled network. The crystal structure of *N,N'*-bis(salicylidene)-1,5-diethylenetriamine rare earth metal ion complexes is made of the neutral dimeric units involving the deprotonated ligand with N_3O_2 donor set, with the voids which are filled with the disordered solvent molecules. Their bonding properties influence the resulting supramolecular architecture. In both types of these complexes the metal ions are eight coordinated with distorted square antiprism geometry. The metal ions are bonded to all the potential nitrogen and oxygen donor atoms of the deprotonated ligands. This type of coordination is in a marked contrast to the neutral exclusively O–donor type of coordination observed in related salicylaldimine lanthanide complexes [17-21]. These results confirm the effectiveness of rare earth elements in self-assembly of the components leading to the formation of compounds with unusual structures, although the final product of this process may be difficult to predict.

Appendix A. Supplementary data

Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre, Nos. CCDC 144775 (**1**), CCDC 1447755 (**1a**), CCDC 1447756 (**2**), CCDC 1447757 (**3**) and CCDC 1447758 (**4**) . Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(1223)336-033, e-mail:deposit@ccdc.cam.ac.uk, or www: http://www.ccdc.cam.ac.uk

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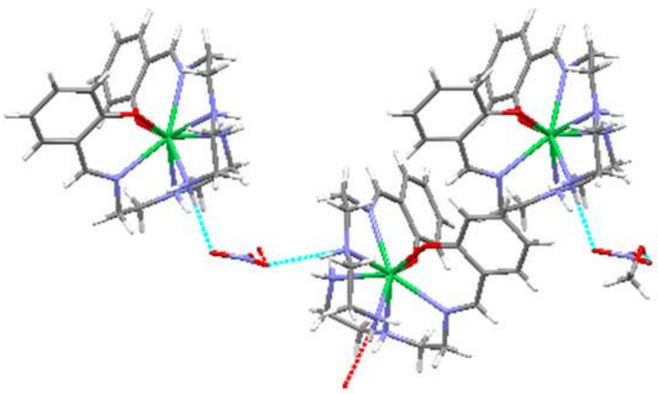
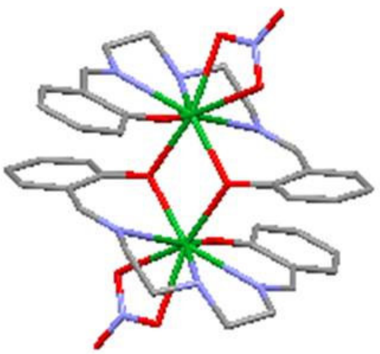


[Tm($C_{11}H_{16}N_3O)_2$]$NO_3\cdot CH_3OH$



[$M_2(C_{18}H_{19}N_3O_2)_2(NO_3)_2$]
M = Y^{3+}, Eu^{3+}or Lu^{3+}

The self-assembled metal-promoted synthesis of salicylaldimine complexes of rare earth metal ions is described. Two types of Schiff base complexes reveal two different supramolecular architectures: a monomer in $[Tm(C_{11}H_{16}N_3O)_2]NO_3 \cdot CH_3OH$ complex with formations of a two-dimensional network and a dimer in $[M_2(C_{18}H_{19}N_3O_2)_2(NO_3)_2]$ complexes (M = Y^{3+}, Eu^{3+}or Lu^{3+}). The complexes contain *N*-(salicylidene)-diethylenetriamine deprotonated ligand with N_3O set of donor atoms or *N,N'*-bis(salicylidene)-diethylenetriamine deprotonated ligand with N_3O_2 donor system.

- Two types of rare earth ion complexes are formed in metal template Schiff base [1+1] or [2+1] condensation of salicylaldehyde and diethylenetriamine.
- The complexes were characterized by spectroscopic methods.
- Solid-state structures were determined by single crystal X-ray diffraction.
- The metal ions are eight-coordinated with a distorted square antiprism geometry.
- The absorption and emission spectra of compounds were studied at room temperature.