

Synthesis, characterization, X-ray structure and photoluminescence properties of two Ce(III) complexes derived from pentadentate ligands



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ARTICLE INFO

Article history:

Received 4 June 2015

Received in revised form

5 August 2015

Accepted 5 August 2015

Available online 7 August 2015

Keywords:

Ce(III) complex

X-ray structure

Spectroscopy

Photoluminescence

ABSTRACT

In this study, two new Ce(III) complexes $[\text{Ce}(\text{L}^1)(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$ and $[\text{Ce}(\text{L}^2)(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$ were synthesized and characterized by spectroscopic and analytical methods where L^1 and L^2 are pentadentate diimine ligands. Molecular structure of $[\text{Ce}(\text{L}^1)(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$ was determined by single crystal X-ray diffraction study. The complex was found to crystallize as $[\text{Ce}(\text{L}^1)(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$. In the complex, the ligand L^1 coordinates to the Ce(III) ion with the N_3O_2 donor set and the Ce(III) ion sits within the cavity of acyclic ligand. The Ce(III) ion is 11-coordinated by three nitrogen atoms from the ligand and eight O atoms, six of which come from three nitrate ions, two from the ligand. In the structure of the complex, water molecules link molecules together to form a 3D hydrogen bond network. Thermal behavior of the Schiff base ligands and their Ce(III) complexes metal complexes were studied under nitrogen atmosphere in the temperature range of 20–800 °C. Thermal stability of the ligands increased upon complexation with Ce(III) ion. In the UV–Vis spectra of Ce(III) complexes, new absorption bands appeared at 340–450 nm and these new bands were attributed to metal–ligand (M–L) charge transitions. Photoluminescence properties of the ligands and their Ce(III) complexes were examined.

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1. Introduction

The nitrogen-oxygen containing multidentate ligands and their metal complexes are of special interest due to their potential applications in several fields including catalysis, transport processes and modeling of several biological compounds [1–10]. Schiff base compounds are used as ligands in metal coordination chemistry and metal complexes derived from Schiff bases have occupied a central role in the development of coordination chemistry [11–15]. There are a number of publications on Schiff base metal complexes regarding their antimicrobial activity, thermal studies, electrochemical properties, as electrochemical sensors and as catalysts for epoxidation of olefins, lactide polymerization, ring opening of epoxides and Michael reactions [16–18].

Trivalent lanthanide complexes have received considerable attention due to their interesting magnetism [19,20], luminescent properties [21] and potential applications including Ln-doped

semiconductors [22], fluorescent [23], magnetic [24], catalytic [25], and nonlinear optical materials [26]. Lanthanide complexes usually exhibit high coordination numbers and structural diversity [27,28]. The relatively large size of the lanthanide ions usually allows accommodation of more than six donor atoms. The solid-state coordination numbers and geometries of lanthanides are difficult to predict, especially for complexes of mono- and bi-dentate ligands [28]. Several mono- and poly-nuclear lanthanide complexes of Schiff base ligands derived from 2,6-diacetylpyridine or 2,6-diformylpyridine with polydentate hydrazones, semicarbazones, and thiosemicarbazones were reported in literature [29–35].

In our previous study, the synthesis, structural characterization, electrochemical and luminescence properties of a La(III) complex were investigated [28]. Due to the importance of lanthanide complexes and in continuance of our interest in the synthesis of trivalent lanthanide, we herein reported the synthesis, spectral, electrochemical and luminescence properties of two pentadentate Schiff base ligands (Fig. 1) and their Ce(III) complexes. The structure of the ligands and their Ce(III) complexes were characterized by spectroscopic and analytical methods. Molecular structure of $[\text{Ce}(\text{L}^1)(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$ was determined by single crystal X-ray diffraction study.

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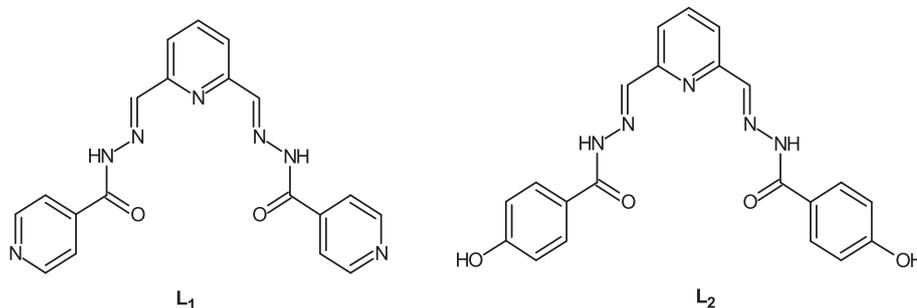


Fig. 1. Proposed structures of synthesized ligands.

2. Experimental

2.1. Materials

All starting materials and organic solvents were purchased from commercial sources and used as received unless otherwise noted. 2,6-Diformylpyridine was prepared by oxidation of 2,6-pyridinedimethanol using manganese dioxide according to the literature method [36].

2.2. Physical measurements

FT-IR spectra were performed using KBr pellets on a Perkin Elmer Paragon 1000PC. CHN analysis was performed using a CE-440 Elemental analyser. The ^1H and ^{13}C NMR spectra were performed on a Bruker Avance 500. ESI mass spectra were recorded on an ESI/MS Tandem mass spectrometry. The electronic spectra in the 200–900 nm range were obtained on a Shimadzu UV-1800 UV–Vis spectrophotometer. The single-photon fluorescence spectra were collected on a Varian Cary Eclipse fluorescence spectrometer.

Data collection for X-ray crystallography was completed using a Bruker APEX2 CCD diffractometer and data reduction was performed using Bruker SAINT. SHELXS97 was used to solve and SHELXL2014/6 to refine the structure [37].

2.3. Synthesis of ligands L^1 and L^2

Pyridine-4-carbohydrazide or 4-hydroxybenzohydrazide (10 mmol) was added to a solution of 2,6-diformylpyridine (5 mmol) in MeOH (20 ml). Resulting solution was then refluxed for 4 h. Upon cooling to the room temperature, a white precipitate formed was filtered and dried in air.

L^1 : color: white, Yield: %92, Elemental analysis: Calc. for $\text{C}_{19}\text{H}_{15}\text{N}_7\text{O}_2 \cdot 2\text{H}_2\text{O}$ (F.W.:409.398): C, 55.74; H, 4.68; N, 23.95. Found: C, 54.93; H, 4.45; N, 23.18%. ^1H NMR (DMSO- d_6 as solvent, δ in ppm); 11.92 (s, 2H, NH), 10.44 (s, 2H, OH), 8.64 (s, 2H, CH=N), 7.99 (t, 1H, CH pyridine), 7.93 (d, 2H, CH pyridine), 7.84 (d, 4H, CH aromatic), 6.94 (d, 4H, CH aromatic). ^{13}C NMR (DMSO- d_6 as solvent, δ in ppm); 163.46 (C=O), 160.25 (C=N), 148.15, 136.78, 129.38, 122.10, 119.62, 114.65 (aromatic). IR (KBr, cm^{-1}): 3401, 3104, 2891, 1662, 1603, 1554, 1492, 1455, 1410, 1322, 1298, 1221, 1146, 1061, 992, 963, 887, 842, 799, 746, 675. Mass spect(ESI): m/z 396(40%) [$L^1+\text{Na}$] $^+$, 279(100%) [$\text{C}_{14}\text{H}_{11}\text{N}_6\text{O}$] $^+$.

L^2 : color: white, Yield: %95, Elemental analysis: Calc. for $\text{C}_{21}\text{H}_{17}\text{N}_5\text{O}_4 \cdot 2\text{H}_2\text{O}$ (F.W.:439.421): C, 57.40; H, 4.82; N, 15.94. Found: C, 57.11; H, 4.48; N, 15.21%. ^1H NMR (DMSO- d_6 as solvent, δ in ppm); 11.94 (s, 2H, NH), 10.24 (s, 2H, OH), 8.59 (s, 2H, CH=N), 7.94 (t, 1H, CH pyridine), 7.96 (d, 2H, CH pyridine), 7.86 (d, 4H, CH aromatic), 6.91 (d, 4H, CH aromatic). ^{13}C NMR (DMSO- d_6 as solvent,

δ in ppm); 163.58 (C=O), 161.40 (C=N), 153.85 (C–OH), 147.12, 137.98, 130.36, 124.00, 120.62, 115.59 (aromatic). IR (KBr, cm^{-1}): 3502, 3222, 3073, 1629, 1606, 1577, 1557, 1512, 1492, 1456, 1362, 1325, 1264, 1174, 1107, 1075, 927, 901, 847, 804, 761, 673. Mass spect(ESI): m/z 426(100%) [$L^2+\text{Na}$] $^+$.

2.4. Synthesis of the Ce(III) complexes

To a stirring solution of the ligands (1 mmol) in MeOH (20 ml), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1 mmol) was added and the reaction solution was refluxed for 4 h. Clear orange solution was left for air evaporation. After two days, an orange powder formed was collected by filtration and dried in air. Single crystals of $[\text{Ce}(\text{L}^1)(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$ suitable for X-ray diffraction study were obtained from slow diffusion of diethylether into a MeOH solution of the complex.

$[\text{Ce}(\text{L}^1)(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$: Orange, Yield:%78, Elemental analysis: Calc. for $\text{C}_{19}\text{H}_{17}\text{N}_{10}\text{O}_{12}\text{Ce}$ (F.W.:717.51): C, 31.80; H, 2.39; N, 19.52. Found: C, 31.11; H, 2.14; N, 18.95%. IR (KBr, cm^{-1}): 3495, 2984, 1644, 1573, 1554, 1481, 1445, 1379, 1280, 1166, 1108, 1089, 1066, 1027, 951, 925, 852, 817, 734, 693, 547, 520. χ_m (MeOH, 10^{-3} M): $4.25 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$.

$[\text{Ce}(\text{L}^2)(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$: color: Orange, Yield: %80, Elemental analysis: Calc. for $\text{C}_{21}\text{H}_{17}\text{N}_8\text{O}_{13}\text{Ce}$ (F.W.:747.53): C, 33.74; H, 2.56; N, 14.99. Found: C, 33.12; H, 2.21; N, 14.31%. IR (KBr, cm^{-1}): 3243, 3074, 1620, 1601, 1581, 1557, 1507, 1456, 1373, 1293, 1263, 1180, 1115, 1033, 943, 914, 850, 758, 742, 692, 624, 550, 523. χ_m (MeOH, 10^{-3} M): $5.48 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$.

2.5. X-ray structure solution and refinement

Data for complex $[\text{Ce}(\text{L}^1)(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$ was collected at 150(2) K on a Bruker ApexII CCD diffractometer using Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data reduction was performed using Bruker SAINT [38]. The structure was solved by direct methods and refined on F^2 using all the reflections. All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters and hydrogen atoms bonded to carbon atoms were inserted at calculated positions using a riding model. The crystal used in the measurement was a racemic twin, with approximately equal twin components. Hydrogen atoms bonded to the nitrogen atom (N3) and water molecule (O7) were located from difference maps and refined with temperature factors riding on the carrying atoms. One of the nitrate ions in the structure is highly disordered and this was modeled over two positions. Details of the crystal data and refinement are given in Table 1.

3. Result and discussion

In this work, two pentadentate Schiff base ligands and their Ce(III) complexes were prepared and characterized by

Table 1
Crystallographic data for the Ce(III) complex.

Empirical formula	C ₁₉ H ₁₇ CeN ₁₀ O ₁₂
Formula weight	717.55
Crystal size (mm ³)	0.27 × 0.25 × 0.04
Crystal color	Yellow
Crystal system	Monoclinic
Space group	C2
Unit cell <i>a</i> (Å)	10.7314(14)
<i>b</i> (Å)	13.3180(18)
<i>c</i> (Å)	10.4986(14)
α (°)	90
β (°)	115.1852(17)
γ (°)	90
Volume (Å ³)	1357.8(3)
Z	2
Abs. coeff. (mm ⁻¹)	1.755
Refl. collected	6221
Completeness to $\theta = 28.33^\circ$	99.6%
Ind. Refl. [R _{int}]	3278 [0.0272]
R1, wR2 [I > 2 σ (I)]	0.0338, 0.0751
R1, wR2 (all data)	0.0351, 0.0761
CCDC number	1404489

spectroscopic and analytical methods. Elemental analysis data of the ligands and their Ce(III) complexes are well agreed with the theoretical values. The purity of the ligands was checked by elemental analysis, ¹H–¹³C NMR spectra and ESI mass spectrum. In the ¹H NMR spectra of the ligands, azomethine group hydrogen atoms were observed at δ 8.64 and 8.59 ppm for L¹ and L², respectively. Broad signals at δ 11.92 and 11.94 ppm are due to the NH group protons. In ¹H spectrum of L², phenolic protons (Ph-OH) were observed at δ 10.24 ppm. Aromatic proton signals were seen at δ 7.99–6.94 ppm range for both ligands. In the ¹³C NMR spectra of the ligands, the number of carbon atom signals is well agreed with their proposed structures. The carbon atoms of the carbonyl groups (C=O) were observed at δ 163.58 and 163.46 ppm, for L¹ and L², respectively. The azomethine group carbon atom signals were seen at δ 161.40 and 160.25 ppm, for L¹ and L², respectively. All the other carbon atoms signals for both ligands were shown in the range of δ 148.15 and 114.65 ppm. ¹H and ¹³C NMR spectra of L² are given in Fig. S1 and Fig. 2, respectively.

Two mononuclear Ce(III) complexes were prepared by the reaction of one equivalent Schiff base ligand and one equivalent Ce(NO₃)₃·6H₂O in a refluxing MeOH solution. The orange colored complexes are stable at room temperature in the solid state without decomposition. The complex is soluble in common organic solvents such as MeOH, EtOH, acetonitrile, DMF and DMSO, partially soluble in chloroform and dichloromethane, not soluble in diethylether. The formation of the Schiff base ligands and their Ce(III) complexes is supported by IR spectroscopy. The IR spectra of the Ce(III) complexes taken in the 4000–450 cm⁻¹ region are very similar to one another suggesting the same bonding fashion of the ligands in these complexes. The infrared spectral data of the ligands and their Ce(III) complexes are given in the experimental section, IR spectra of the ligand L¹ and its Ce(III) complex are shown in Figs. 3 and 4, respectively, and rest of the IR spectra of L² and its Ce(III) complex are given in supplementary file (Figs. S2&S3). In the IR spectra of the ligands L¹ and L², the sharp bands at 1662 and 1629 cm⁻¹ were assigned to $\nu_{(C=O)}$ vibrations, respectively. The broad bands in the range of 3502 and 3104 cm⁻¹ were can be assigned to $\nu_{(O-H)}$ and $\nu_{(N-H)}$ stretches, respectively. In the spectra of the Schiff base ligands, characteristic azomethine $\nu_{(CH=N)}$ vibration was observed at 1603 and 1606 cm⁻¹, for L¹ and L², respectively. In the spectra of the complexes [Ce(L¹)(NO₃)₃]·H₂O and [Ce(L²)(NO₃)₃]·H₂O azomethine $\nu_{(CH=N)}$ and carbonyl group $\nu_{(C=O)}$ vibrations shifted toward lower wavenumbers confirming coordination of azomethine

nitrogen and carbonyl oxygen atoms with the Ce(III) ion. The nitrate group stretching frequencies were observed as split bands at the 1444–1280 cm⁻¹ suggesting at least one of three nitrate ions coordination to the metal as a bidentate ligand. X-ray structure analysis of [Ce(L¹)(NO₃)₃]·H₂O showed that all three nitrate ions bind to Ce(III) as bidentate chelating ligands. The occurrence of the bands at 520–547 and 523–550 cm⁻¹ for [Ce(L¹)(NO₃)₃]·H₂O and [Ce(L²)(NO₃)₃]·H₂O associated with Ce–O and Ce–N vibrations, respectively, supports the involvement of the nitrogen and oxygen atoms in the coordination sphere of Ce(III) ions.

The ESI spectrum of the ligands and their Ce(III) complexes were investigated in MeOH. The ESI mass spectrum of the ligands (L¹ and L²) showed signals at *m/z* 396(40%) and 426(100%) assigned to molecular ion signals for [L¹+Na]⁺ and [L²+Na]⁺, respectively (Figs. S4&S5). The mass spectra of the complexes show several fragmentation signals and molecular ion signals were not observed for the complexes.

Molar conductance value of the complexes [Ce(L¹)(NO₃)₃]·H₂O and [Ce(L²)(NO₃)₃]·H₂O in MeOH (10⁻³ M) were found to be 4.25 and 5.48 $\Omega^{-1}cm^2mol^{-1}$, respectively, indicating the nonelectrolyte nature of the complexes in MeOH solution. The conductivity results of the complexes show that the nitrate ions are present in the coordination sphere in MeOH solution.

Thermal behavior of the Schiff base ligands and their Ce(III) complexes metal complexes were studied under nitrogen atmosphere in the temperature range of 20–800 °C. The thermal curve for the complex [Ce(L¹)(NO₃)₃]·H₂O is shown in Fig. 5 and rest of the spectra are given in the supplementary file (Figs. S6–S8). The TG curve of L¹ shows three decomposition steps and the molecular backbone of the compound is thermally stable up to about 200 °C. The first decomposition stage appeared at 30–150 °C for Cu(II) complex, with a mass loss 3.54%, accompanied by an endothermic peak with *T*_{max} = 110 °C on the DTA curve, may be attributed to the removal of absorbed two molecules of water. In the second decomposition step approximately 65.26% of the other organic moiety decomposed within the temperature range of 200–600 °C with an endothermic peak in this region (*T*_{max} = 280 °C). Rest of the organic residue decomposes gradually up to high temperature. The complex [Ce(L¹)(NO₃)₃]·H₂O is thermally more stable than its free ligand L¹. Thermal decomposition of the complex also contains three decomposition steps. In the first decomposition step, a water molecule in the structure was lost in the range of 30–150 °C. The structure of the complex is stable up approximately 220 °C. In the second step of thermal decomposition, about 44.63% mass of the complex was lost in the range of 220–400 °C accompanied by an endothermic peak with *T*_{max} = 290 °C. Rest of the organic residue of the complex was lost between 400 and 700 °C. No further weight loss was observed above 700 °C leaving metal oxides as a final residue (CeO₂, Ce₂O₃).

The thermal decomposition of the ligand L² starts at around 300 °C and approximately 35.04% of mass was lost in the range of 200–550 °C with an endothermic peak in this region (*T*_{max} = 360). Thermal decomposition of the ligand continues up to high temperatures (>800 °C). Thermal study indicated that the ligand L² is thermally more stable than L¹. This may be due to two extra phenolic groups present involved in hydrogen bonding with neighboring molecules increasing the thermal stability. The complex [Ce(L²)(NO₃)₃]·H₂O showed about 3.28% weight loss in the range of 30–150 °C due to an absorbed water molecule in the structure. Approximately half of the total mass was lost between 320 and 500 °C. Also, the DTA curve shows an endothermic peak at *T*_{max} = 365 °C in this region. Rest of the organic moiety was gradually removed from the structure up to 800 °C and no further weight loss was observed above this temperature leaving about 28% of total mass as a final residue (metal oxides CeO₂, Ce₂O₃).

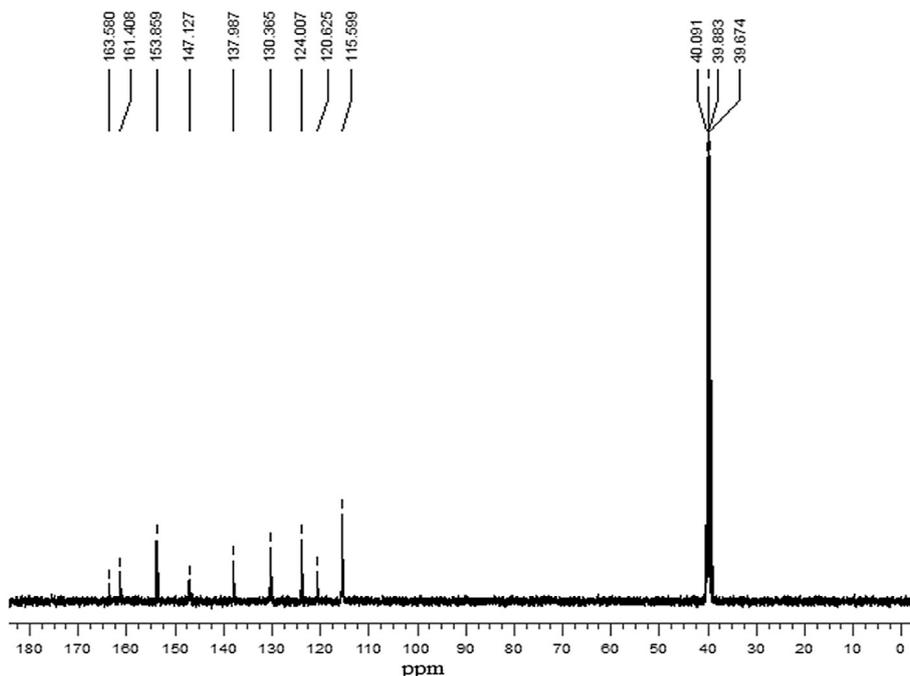


Fig. 2. ^{13}C NMR spectrum of L^2 .

3.1. X-ray structure of complex $[\text{Ce}(\text{L}^1)(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$

Single crystals of the complex suitable for X-ray diffraction study were obtained by slow evaporation of a MeOH solution of the complex. The complex was found to crystallize as $[\text{Ce}(\text{L}^1)(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$. The complex crystallizes in monoclinic crystal system, $P2_1/n$

space group with unit cell parameters $a = 10.7314(14)$, $b = 13.3180(18)$, $c = 10.4986(14)$ Å, $\beta = 115.1852(17)^\circ$, $V = 1357.8(3)$ Å³ and $Z = 2$. The complex lies across a twofold crystallographic axis with the Ce1, N1, C1, N5, O5, O6 atoms sitting on this axis. Molecular structure of the complex molecule is shown in Fig. 6. All bond lengths and angles are within the normal ranges. Selected bond

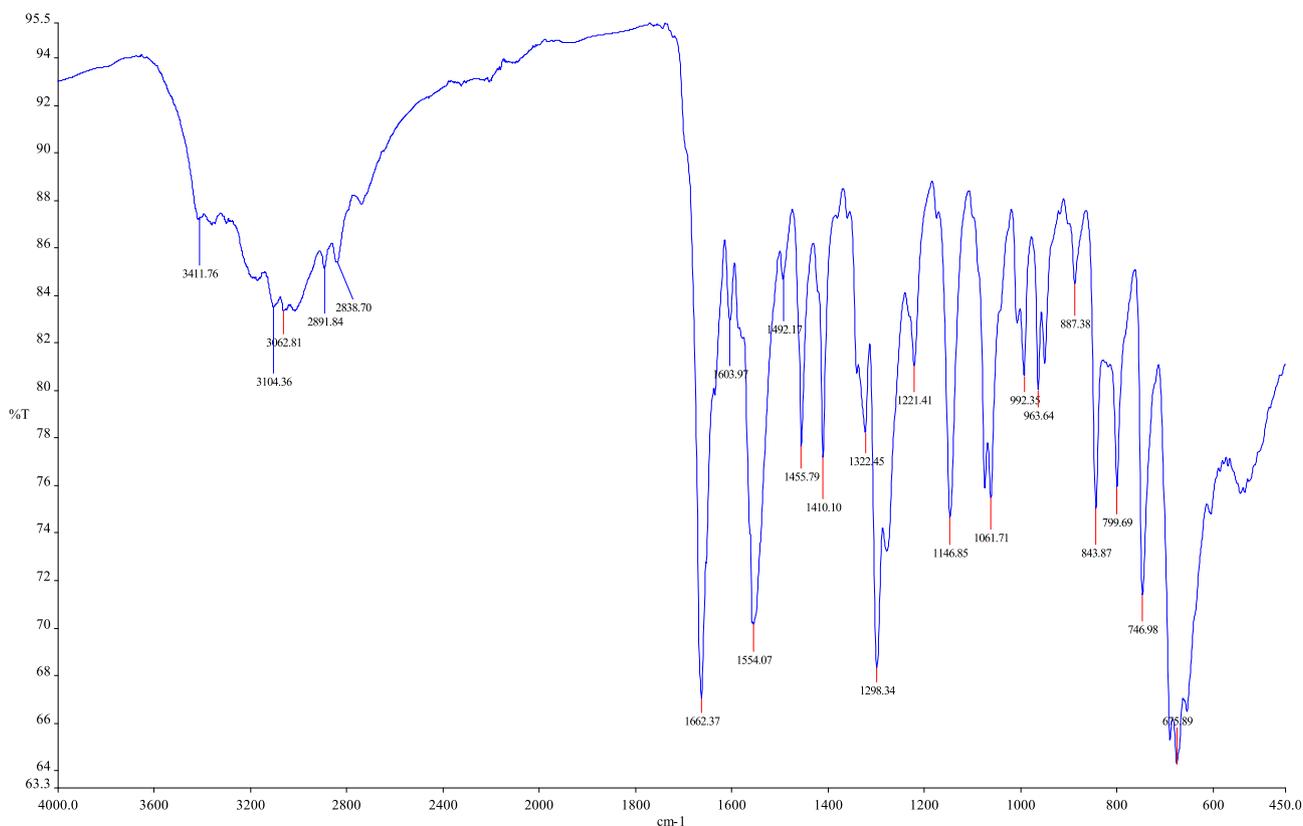


Fig. 3. FTIR spectrum of L^1 .

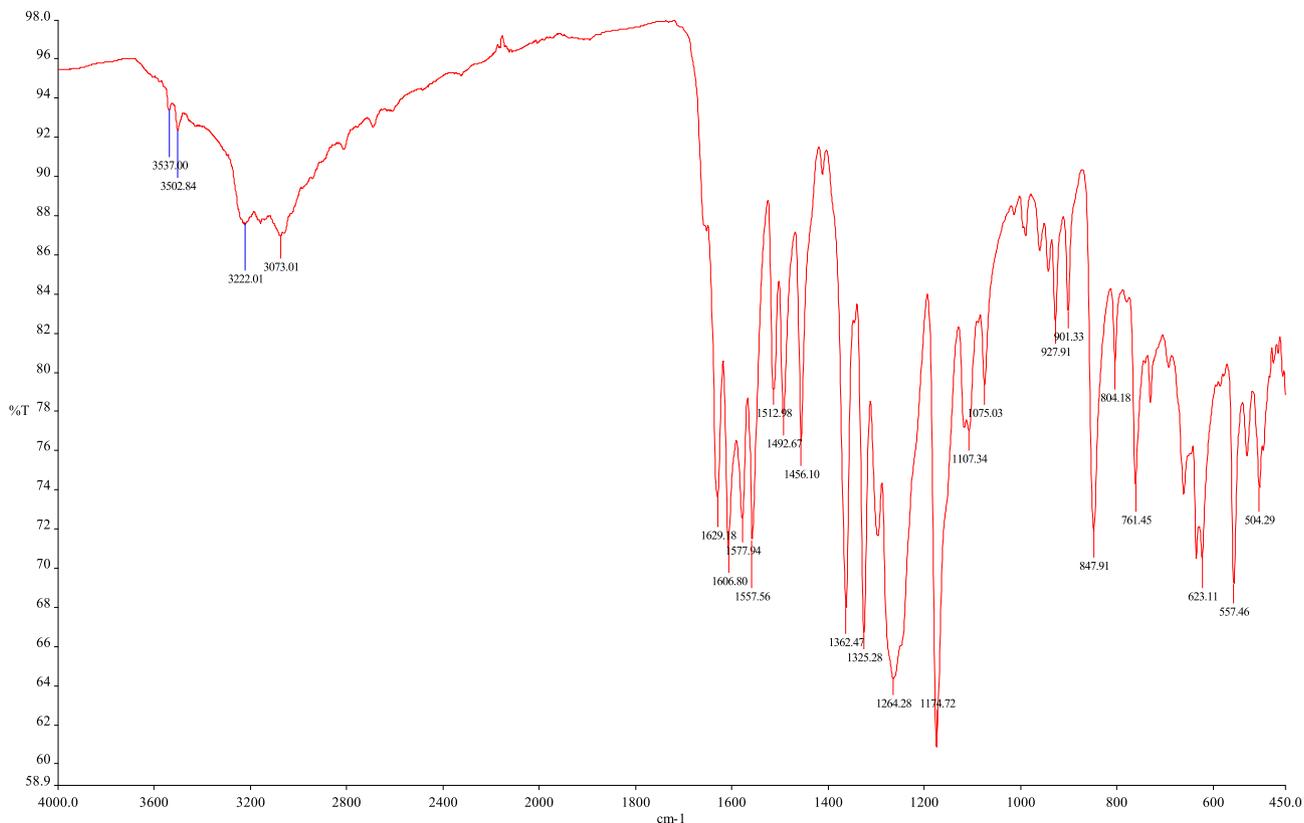


Fig. 4. FTIR spectrum of $[\text{Ce}(\text{L}^1)(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$.

lengths are listed in Table 2. In the complex, each Ce(III) ion is 11-coordinated and the ligand bind to the Ce(III) ion with N_3O_2 donor set group (two imine nitrogen, one pyridine nitrogen and two carbonyl group oxygen atoms). All three nitrate ions coordinate

to the metal ion as bidentate ligands. The Ce–O bond distances are longer than the Ce–N bond distances as expected. The N2–C4 and O1–C5 distances of 1.256(13) and 1.261(17) Å exhibits a typical C=N and C=O double bond characters respectively.

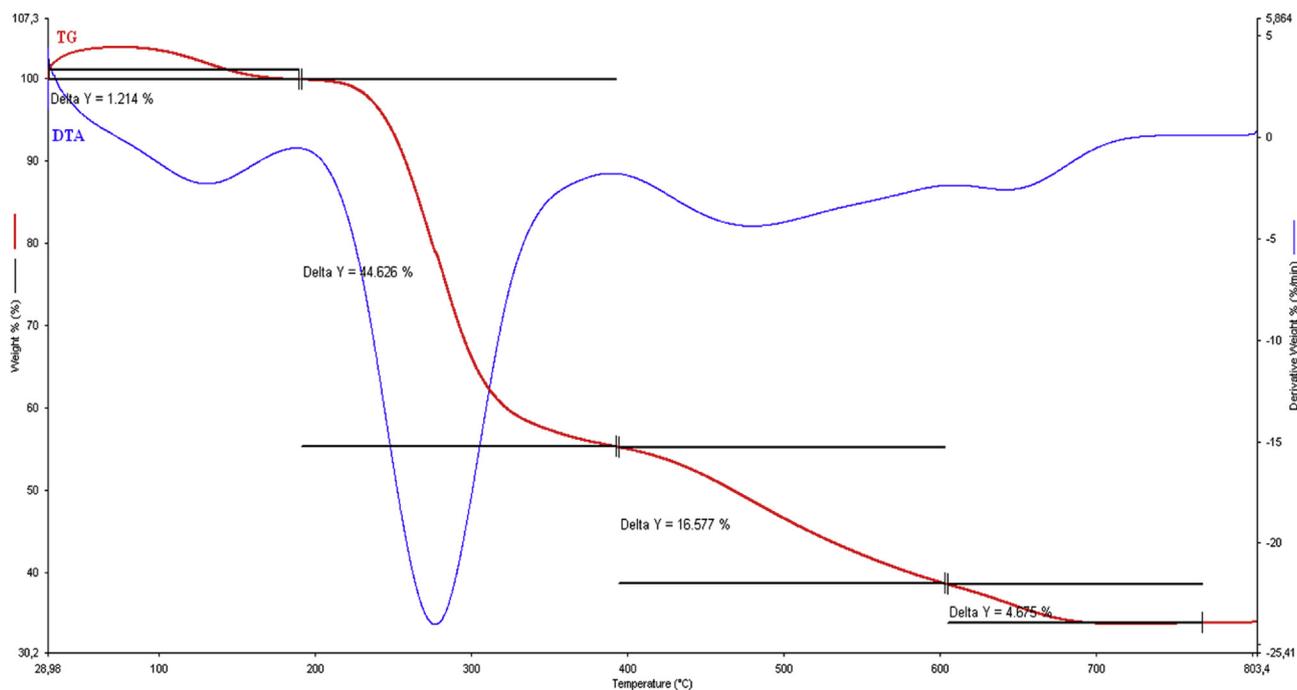


Fig. 5. Thermal curves for $[\text{Ce}(\text{L}^1)(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$.

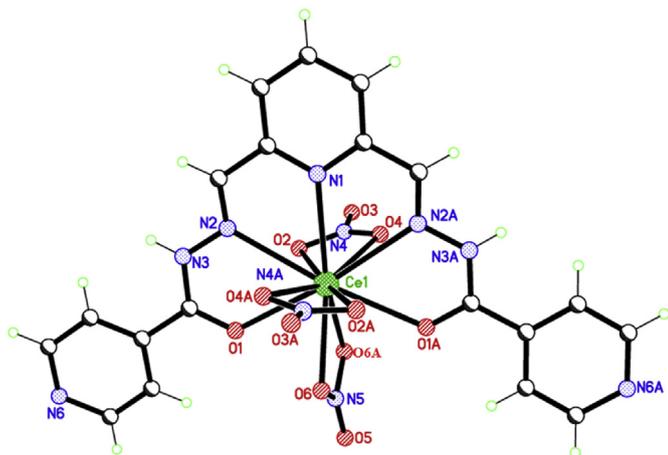


Fig. 6. Molecular structure of the complex $[\text{Ce}(\text{L}^1)(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$.

Water molecules in the structure make two types of hydrogen bonding linking complex molecules. First, water molecules involve in hydrogen bonding with one of the oxygen atom of a nitrate ion and pyridine nitrogen atom as donor. Second, NH group of the ligand makes intermolecular hydrogen bond with water molecule ($\text{NH} \cdots \text{OH}_2$). These intermolecular hydrogen bonding contacts are extended between the other symmetry-related molecules in their respective planes to form a 3D hydrogen bond network (Fig. 7). Hydrogen bond parameters are listed in Table 3. Hydrogen bonded complex molecules further connected with π - π interactions. The C1–C2 atoms of central pyridine ring are stacked with the C5*–C6* section of an adjacent molecule under symmetry operation of $3/2 - x, 1/2 + y, 2 - z$. The C1–C5* and C2–C6* atoms are separated by distances of 3.493 and 3.447 Å, respectively. These interactions are shown in Fig. 8.

3.2. UV–Vis and photoluminescence properties

The UV–Vis absorption spectra of the Schiff base ligands and their Ce(III) complexes were investigated in the range of 200–800 nm in MeOH (10^{-4} M) (Fig. S9). Absorption spectra of both ligands L^1 and L^2 show only one absorption band in the 250–350 nm range and this was assigned to the π - π^* transitions of the ligands. In the absorption spectra of the complexes these π - π^* transition shifted to lower wavelength values (red shift). In the spectra of Ce(III) complexes, new absorption bands appeared at 340–450 nm and these new bands were attributed to metal–ligand (M–L) charge transfer. No metal induced transitions were observed at the concentrations studied.

The photoluminescence spectra for the Schiff base ligands and their Ce(III) complexes investigated at room temperature on a Varian Cary Eclipse fluorescence spectrometer. All samples were prepared in MeOH and analyzed in a 1 cm optical path quartz cuvette [39]. The emission and excitation spectra of the ligands and metal complexes L^1 and L^2 in MeOH (10^{-5} M) are shown in Fig. 9 and the obtained data are given in Table 4.

In the excitation spectra of the L^1 ligand in MeOH, one excitation

Table 2
Selected bond lengths [Å] for $[\text{Ce}(\text{L}^1)(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$.

Ce(1)–O(1)	2.625(6)	Ce(1)–O(4)	2.569(4)
Ce(1)–N(2)	2.747(8)	Ce(1)–O(6)	2.57(3)
Ce(1)–N(1)	2.765(11)	O(1)–C(5)	1.261(12)
Ce(1)–O(2)	2.580(4)	N(2)–C(4)	1.256(10)

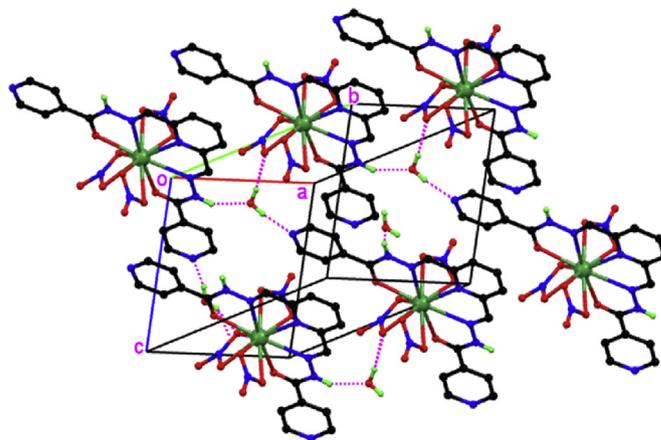


Fig. 7. Packing diagram of $[\text{Ce}(\text{L}^1)(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$ showing hydrogen bond network. Hydrogen atoms bonded to carbon atoms are not shown for clarity.

Table 3
Hydrogen bonds for $[\text{Ce}(\text{L}^1)(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$ [Å and °].

D–H ... A	d(D–H)	d(H ... A)	d(D ... A)	<(DHA)
N(3)–H(3) ... O(7) ⁱ	0.88	2.04	2.849(11)	152.3
O(7)–H(7B) ... O(6) ⁱⁱ	0.84	1.99	2.80(3)	163.4
O(7)–H(7B) ... O(6A) ⁱⁱ	0.84	2.04	2.80(3)	152.2
O(7)–H(7A) ... N(6)	0.83	1.90	2.700(7)	163.0

i: $-x+1/2, y+1/2, -z+1$ *ii*: $x-1, y, z-1$.

band was shown in the 300–350 nm range. Excitation at 320 nm caused the Schiff base ligand L^1 to emit at an emission maximum of 547 nm (Fig. 9). This emission can be attributed to π - π^* transitions of the ligand. In the spectra of the complex $[\text{Ce}(\text{L}^1)(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$, both excitation and emission bands shifted to shorter wavelengths (hypsochromic effect). Although, there is no change in the intensity of excitation bands of the ligand L^1 and $[\text{Ce}(\text{L}^1)(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$, emission intensity of the complex shifted to higher values. The complexation of Ce(III) ion with L^1 effected some electrons of atoms or component of the ligand. The ligand L^2 and $[\text{Ce}(\text{L}^2)(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$ complex exhibit similar excitation and emission spectra to the ligand L^1 and its Ce(III) complex. Both the ligand L^2 and $[\text{Ce}(\text{L}^2)(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$ complex show an emission band at 500–550 nm range upon excitation at 280–350 nm. The excitation and emission spectra of L^2 show no significant change upon complexation with Ce(III) ion (Fig. 9).

The effect of the solution concentration on photoluminescence properties were studied (1×10^{-5} – 1×10^{-7} M) (Figs. S10&S11). The emission wavelengths of the ligands their Ce(III) complexes were shifted to lower and higher values when different

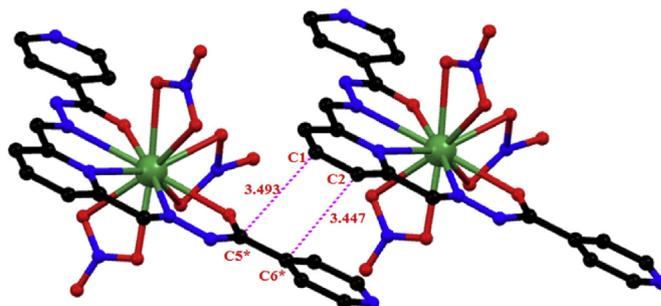


Fig. 8. π - π interactions within the structure of $[\text{Ce}(\text{L}^1)(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$. Hydrogen atoms are not shown for clarity.

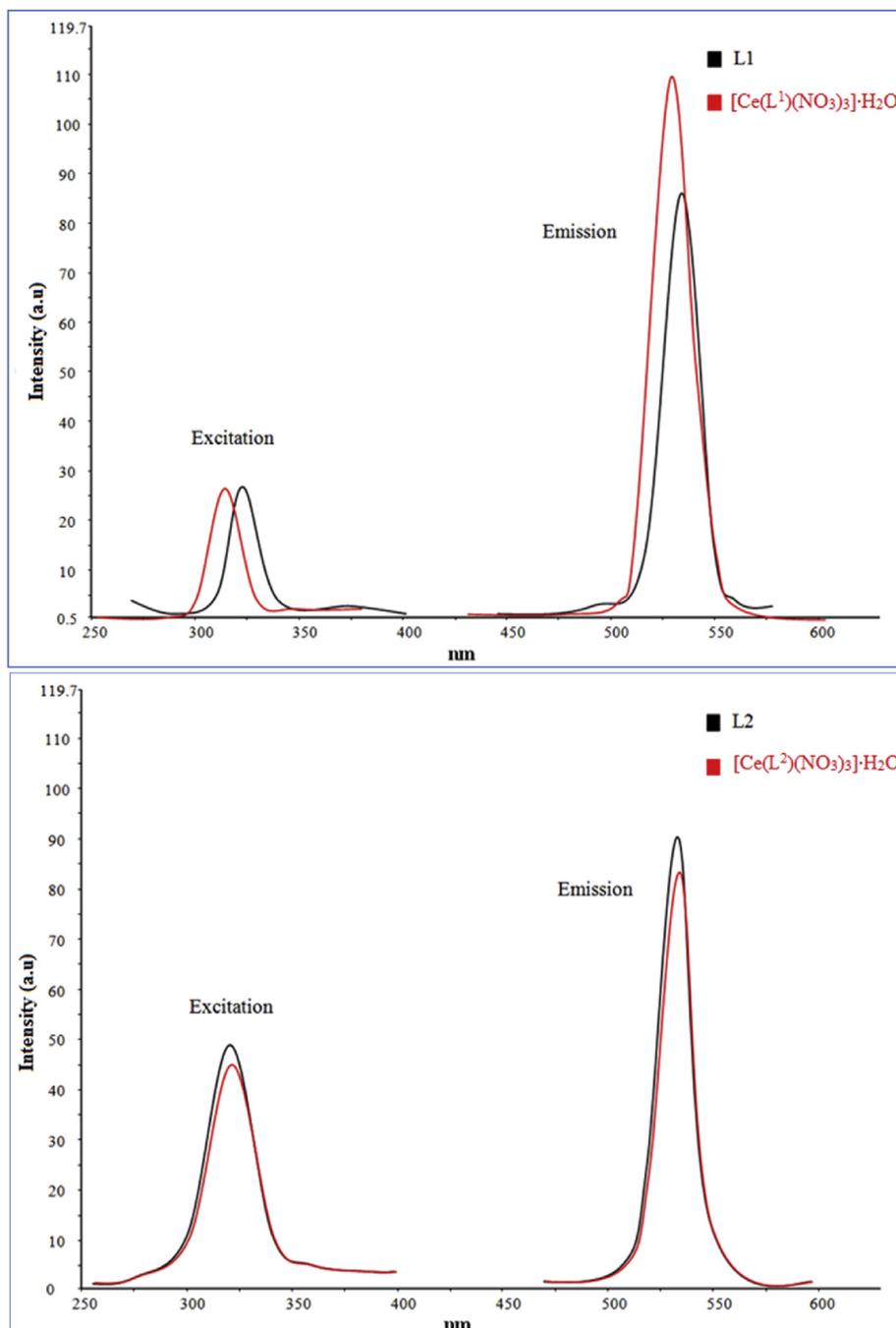


Fig. 9. Excitation and emission spectra of the ligands and their Ce(III) complexes.

Table 4
Photoluminescence data for the synthesized compounds.

	(λ_{\max})					
	1×10^{-5}		1×10^{-6}		1×10^{-7}	
	Exc.	Em.	Exc.	Em.	Exc.	Em.
L ¹	320	547	325	550	310	555
[Ce(L ¹)(NO ₃) ₃]·H ₂ O	300	525	305	570	320	571
L ²	325	550	320	568	324	545
[Ce(L ²)(NO ₃) ₃]·H ₂ O	326	526	320	525	332	518

Exc: Excitation Em: Emission.

concentrations were used. The emission intensities shifted to higher values when concentrations increased from 1×10^{-7} to 1×10^{-5} M. In the spectrum of the ligand L¹, the increase in the concentration results in a blueshift in the emission band.

4. Conclusion

In this study, two pentadentate Schiff base ligand and their Ce(III) complexes were synthesized. The structures of the synthesized compounds were characterized by analytical and spectroscopic methods. Molecular structure of complex [Ce(L¹)(NO₃)₃]·H₂O was determined by single crystal X-ray diffraction technique. In the complex, the Ce(III) ion is 11-coordinated by eight O atoms,

six of which come from three nitrate ions, two from the Schiff base ligand. The ligand L¹ behaves as pentadentate ligand with N₃O₂ donor set group (two imine nitrogen, one pyridine nitrogen and two carbonyl group oxygen atoms) and the Ce(III) sits in the acyclic cavity. Excitation and emission spectra of the prepared compounds were studied.

Supplementary information

CCDC 1404489 contains the supplementary crystallographic data for the complex. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing (data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre 12 Union Road Cambridge CB2 1EZ, UK. Fax: +44(0)1223-336033.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.molstruc.2015.08.016>.

References

- [1] C. Benelli, D. Gatteschi, *Chem. Rev.* 102 (2002) 2369–2388.
- [2] A.D. Sherry, C.F.G.C. Geraldes, Lanthanide probes in life: chemical and earth sciences, in: G.R. Choppin (Ed.), *Theory and Practice*, vol. 93, Elsevier, Amsterdam, The Netherlands, 1989.
- [3] A. Døssing, *Eur. J. Inorg. Chem.* 8 (2005) 1425–1434.
- [4] M. Taniguchi, K. Takahei, *J. Appl. Phys.* 73 (1993) 943–947.
- [5] A. Bencini, C. Benelli, A. Caneschi, R.L. Carlin, A. Dei, D. Gatteschi, *J. Am. Chem. Soc.* 107 (1985) 8128–8136.
- [6] J. Lisowski, P. Starynowicz, *Inorg. Chem.* 38 (1999) 1351–1355.
- [7] V. De Zea Bermudez, R.A. S'a Ferreira, L.D. Carlos, C. Molina, K. Dahmouche, S.J.L. Ribeiro, *J. Phys. Chem. B* 105 (2001) 3378–3386.
- [8] C.V.K. Sharma, R.D. Rogers, *Chem. Commun.* 1 (1999) 83–84.
- [9] S. Salehzadeh, M. Bayat, L. Davoodi, R. Golbedaghi, V. Izadkhan, *Bull. Chem. Soc. Ethiop.* 24 (1) (2010) 59–66.
- [10] Z.Y. Yang, R.D. Yang, F.S. Li, K.B. Yu, *Polyhedron* 19 (2000) 2599–2604.
- [11] A.J. Blake, N.R. Champness, P. Hubberstey, W.S. Li, M.A. Withersby, M. Schroder, *Coord. Chem. Rev.* 183 (1999) 117–138.
- [12] P.A. Vigato, S. Tamburini, *Coord. Chem. Rev.* 248 (2004) 1717–2128.
- [13] W. Zhang, J.L. Loebach, S.R. Wilson, E.N. Jacobsen, *J. Am. Chem. Soc.* 112 (1990) 2801–2803.
- [14] P. Pfeiffer, E. Liibbe, T. Tsumaki, *Justus Liebigs Ann. Chem.* 503 (1933) 84–130.
- [15] P.G. Cozzi, *Chem. Soc. Rev.* 33 (2004) 410–421.
- [16] K.C. Gupta, A.K. Sutar, *Coord. Chem. Rev.* 252 (2008) 1420–1450.
- [17] R. Ganguly, B. Sreenivasulu, J.J. Vittal, *Coord. Chem. Rev.* 252 (2008) 1027–1050.
- [18] K.C. Gupta, A.K. Sutar, Chu-Chieh Lin, *Coord. Chem. Rev.* 253 (2009) 1926–1946.
- [19] D.-P. Li, T.-W. Wang, C.-H. Li, D.-S. Liu, Y.-Z. Li, X.-Z. You, *Chem. Commun.* 46 (2010) 2929–2931.
- [20] T.D. Pasatoiu, M. Etienne, A.M. Madalan, M. Andruh, R. Sessoli, *Dalton Trans.* 39 (2010) 4802–4808.
- [21] X. Yang, R.A. Jones, *J. Am. Chem. Soc.* 127 (2005) 7686–7687.
- [22] M. Taniguchi, K. Takahei, *J. Appl. Phys.* 73 (2) (1993) 943–947.
- [23] V. Alexander, *Chem. Rev.* 95 (2) (1995) 273–342.
- [24] A. Bencini, C. Benelli, A. Caneschi, R.L. Carlin, A. Dei, D. Gatteschi, *J. Am. Chem. Soc.* 107 (26) (1985) 8128–8136.
- [25] J. Lisowski, P. Starynowicz, *Inorg. Chem.* 38 (6) (1999) 1351–1355.
- [26] C.V.K. Sharma, R.D. Rogers, *Chem. Commun.* (1999) 83–84.
- [27] S. Salehzadeh, M. Bayat, L. Davoodi, R. Golbedaghi, V. Izadkhan, *Bull. Chem. Soc. Ethiop.* 24 (1) (2010) 59–66.
- [28] M. Köse, G. Ceyhan, E. Atci, V. McKee, M. Tümer, *J. Mol. Struct.* 1088 (2015) 129–137.
- [29] N.A. Bailey, C.O.R. Barbarin, D.E. Fenton, Y.-S. Ho, G.J. Humber, *Inorg. Chim. Acta* 232 (1995) 227–230.
- [30] G. Bartkowiak, G. Schroeder, *Inorg. Chem. Commun.* 20 (2012) 54–59.
- [31] B. Singh, T.B. Singh, *Synth. React. Inorg. Met. Org. Chem.* 30 (4) (2000) 583–599.
- [32] M. Kozłowski, R. Kierzek, M. Kubicki, W. Radecka-Paryzek, *J. Inorg. Biochem.* 126 (2013) 38–45.
- [33] S. Xue, L. Zhao, Y.-N. Guo, R. Deng, Y. Guo, J. Tang, *Dalton Trans.* 40 (2011) 8347–8352.
- [34] G.M. Oliveira, A. Machado, G.W. Gomes, J.H.S.K. Monteiro, M.R. Davolos, U. Abram, A. Jagst, *Polyhedron* 30 (2011) 851–859.
- [35] A. Jagst, A. Sanchez, E.M. Vazquez-Lopez, U. Abram, *Inorg. Chem.* 44 (2005) 5738–5744.
- [36] E.P. Papadopolous, A. Jarrar, C.H. Issadorides, *J. Org. Chem.* 31 (1966) 615–616.
- [37] Bruker, APEX2 and SAINT, Bruker AXS Inc, 1998.
- [38] G.M. Sheldrick, *Acta Cryst. Sect. A* 64 (2008) 112–122.
- [39] M. Köse, G. Ceyhan, M. Tümer, I. Demirtas, I. Gönül, V. McKee, *Spect. Chim. Acta Part A* 137 (2015) 477–485.