

Hydrothermal synthesis, crystal structure and luminescence property of a three dimensional Sm(III) coordination polymer with 2,5-pyridinedicarboxylic acid

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MS received 12 August 2015; revised 8 September 2015; accepted 19 September 2015

Abstract. A novel three dimensional coordination polymer [Sm(2,5-pydc)(NO₃)(H₂O)]·(H₂O) (2,5-pydc = 2,5-pyridine dicarboxylate) (**1**) had been synthesized hydrothermally and characterized by elemental analysis, FT-IR and single-crystal X-ray diffraction analysis. This coordination polymer crystallized in the monoclinic space group *P2₁/n* with cell parameters *a* = 9.3610(4) Å, *b* = 8.3498(3) Å, *c* = 16.7159(8) Å, *β* = 106.31(0)°, *V* = 1253.98(184) Å³. Thermogravimetric analysis revealed that complex **1** is stable up to 400°C which on photoexcitation at 365 nm exhibited yellow emission at 583 nm.

Keywords. Hydrothermal synthesis; coordination polymer; X-ray diffraction; samarium (III); luminescence property.

1. Introduction

In the burgeoning field of advanced materials, the coordination polymers or metal-organic frameworks (MOFs) play an prominent role in gas storage, luminescence, drug delivery, catalysis, magnetism and separations.^{1–9} Since last decade immense research has been conducted on MOFs and the number of publications has escalated year after year owing not only to the enormous varieties of structural topologies but also due to wide range of potential applications in the above mentioned fields. In contrast to the nomenclature, MOF materials can be developed by connecting together both metal ions or metal oxides and polytopic organic linkers. Organic linkers with different functionality, i.e. bidentate to polydentate aromatic carboxylates, have been used to develop new MOF materials. The design and construction of coordination networks are influenced by many factors such as coordination geometry of metal ions, nature of the organic linker (length of ligand, bulkiness, bond angles, chirality, etc.), molar ratio of metal to organic linker, pH, temperature, solvent used and the selection of precursor materials.^{10–14} A multifunctional pyridine dicarboxylic acid has the tendency to form discrete 1D chain, 2D layer and 3D porous structures through chelation of nitrogen atom and oxygen atom of the carboxylic group.^{15,16} In addition to the functionality

of organic molecules, hydrothermal synthesis is also one of the exploited techniques to construct the coordination polymers. It is difficult to design coordination complexes with lanthanides as compared to transition metals. The f-block metal ions make a far more attractive choice for creating fascinating molecular topologies with new crystal motifs and novel luminescent properties.¹⁷ In this study, we have presented the synthesis, crystal structure and photoluminescence properties of three dimensional Sm(III) coordination polymer constructed with 2,5-pyridine dicarboxylic acid ligand.

2. Experimental

2.1 Materials and measurements

All chemicals and solvents were of analytical grade and used without any further purification. Sm(NO₃)₃·6H₂O was procured from Acros Organics and 2,5-pyridine dicarboxylic acid from Sigma-Aldrich. The infrared spectrum of the samples was recorded using KBr pellet method on a Perkin Elmer 'spectrum two FT-IR'. The elemental analysis of the complex was done using Perkin Elmer 240C CHN analyzer. TGA/DTA was recorded using Mettler Toledo TGA/DSC-1 in the temperature range of 50–1000°C under N₂ atmosphere at 1 atm and a heating rate of 10°C min⁻¹. The luminescence spectrum of the solid sample was

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recorded using Perkin Elmer LS-55 luminescence spectrometer at room temperature.

2.2 Synthesis of $[Sm(2,5\text{-pydc})(NO_3)(H_2O)] \cdot (H_2O)$ (**1**)

$Sm(NO_3)_3 \cdot 6H_2O$ (0.089 g, 0.2 mmol) and 2,5-pyridine dicarboxylic acid (0.034 g, 0.2 mmol) were added to the mixture of water (10.0 mL) and acetonitrile (2.0 mL) and stirred for few minutes. The resultant solution was heated at 160°C in a teflon lined 23 mL stainless steel autoclave for over three days. The resultant red color crystals were collected by filtration and washed with distilled water. Yield was 0.095 g (77.8%). Anal. calcd. (%) for $C_7H_3N_2O_9Sm$: C, 20.53; H, 0.73; N, 6.84. Found (%): C, 20.48; H, 0.71; N, 6.68.

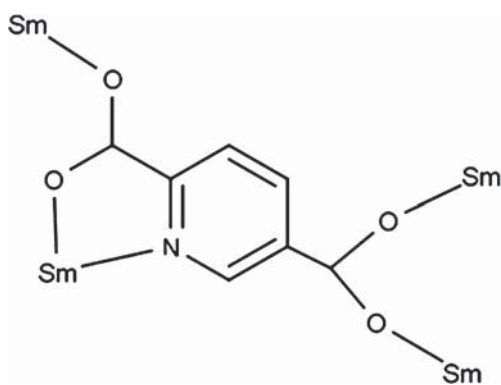
2.3 X-ray structure determination

Single crystal X-ray diffraction data of complex was collected on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. A suitable crystal of the size approximately 30 to 300 microns, selected by using optical microscope, was mounted on

a thin glass fiber. The whole set up was then placed on the goniometer head. Data was collected at 150(2) K using graphite-monochromated Mo K_α radiation ($\lambda_\alpha = 0.71073 \text{ \AA}$). The strategy for the data collection was evaluated by using the CrysAlisPro CCD software. The data was collected by the standard 'phi-omega' scan techniques, and was scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods¹⁸ and refined by full matrix least-squares¹⁹ using SHELXS-97. The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. In X-ray diffraction, the measurement mainly depends upon the existence of electron density. The heavier an atom (more electrons), the stronger is its effect on the diffraction pattern. This means that in the presence of heavy atoms, light atoms like hydrogen are somewhat difficult to localize. Moreover atoms of water molecules must be detected in the experimental electron density or else they get included into the model. So in this crystal structure, we have added four hydrogen atoms to coordinated and uncoordinated water molecules which were not diffracted in X-ray diffraction.²⁰

Table 1. Crystal data, data collection and refinement details of **1**.

Compound	$[Sm(2,5\text{-pydc})(NO_3)(H_2O)] \cdot H_2O$
Empirical formula	$C_7 H_3 N_2 O_9 Sm$
Formula weight	409.46 g/mol
T (K)	150
Wavelength (Å)	1.5418
Space group	P 2/n
a (Å)	9.3610(4)
b (Å)	8.3498(3)
c (Å)	16.7159(8)
α (°)	90.000(0)
β (°)	106.31(0)
γ (°)	90.000(0)
V (Å ³)	1253.98(19)
Z	4
Calculated density (g cm ⁻³)	2.16873
F(000)	771.8
Absorption coefficient (mm ⁻¹)	35.635
Crystal size (mm)	0.33*0.26*0.21
θ range of data collection	4.9161-71.8557
Index range	$-11 \leq h \leq 8, -8 \leq k \leq 10, -19 \leq l \leq 20$
Total reflections	7230
Independent reflections (R_f)	2436
Goodness-of-fit (GOF) on F^2	1.176
Refinement Method	Full-matrix least squares on F^2
Data/restraints/parameter	2436/0/172
R_1 [on $F_o^2, I > 2\sigma(I)$]	0.055
wR_2 [on $F_o^2, I > 2\sigma(I)$]	0.166



Scheme 1. Binding modes of 2,5-pydc ligand in coordination polymer **1**.

3. Results and Discussion

3.1 Crystal structure of $[Sm(2,5\text{-pydc})(NO_3)(H_2O)] \cdot (H_2O)$ (**1**)

The asymmetric unit of **1** contains one crystallographically independent Sm(III) cation, one 2,5-pydc ligand, one nitrate anion, one coordinated and another uncoordinated water molecule. The crystal data and refinement details are presented in table 1. As shown in scheme 1, all coordination sites of 2,5-pydc are involved in bonding with Sm(III) atoms. The X-ray structural analysis of **1** reveals that Sm(III) atom is coordinated with eight oxygen atoms, one nitrogen atom and shows mono-capped square antiprismatic geometry (figure 1a). As depicted in the figure 1b, nine coordination sites on the Sm(III) atom are occupied with five oxygen and one

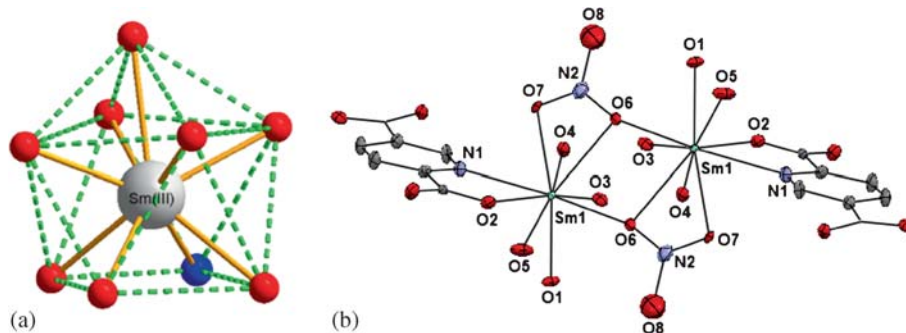


Figure 1. (a) Coordination geometry. (b) ORTEP representation of **1** at the 50% probability level. Symmetry Codes: x, y, z ; $0.5-x, 0.5+y, 0.5-z$; $0.5+x, 0.5-y, 0.5+z$; $-x, -y, -z$.

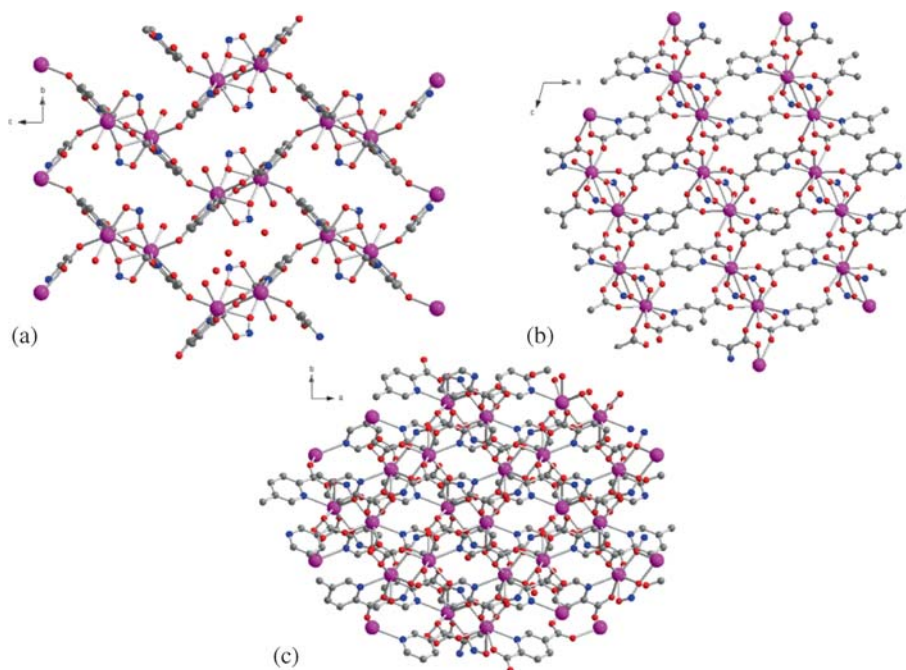


Figure 2. Three-dimensional network of **1** projected along (a) a -axis, (b) b -axis and (c) c -axis.

nitrogen atoms (O1, O2, O3, O4, O5, N1) from four different 2,5-pydc ligands and three oxygen atoms (O6 \times 2, O7) from two nitrate anionic groups. The Sm(III)-O bond distance is found in the range of 2.361 to 2.496 Å and Sm(III)-N bond distance at 2.613 Å. Interestingly, the nitro group chelates with the Sm(III) metal cation through two oxygen atoms (O6 and O7) and forms a four membered chelating ring. Furthermore, two O6 oxygen atoms from two nitro groups form μ -bridged bonding between two successive Sm(III) atoms which leads to generate a dinuclear unit. The distance between two Sm(III) atoms is 4.0294 Å. The completely deprotonated 2,5-pydc ligand is able to interlink the adjacent dinuclear units infinitely in all three directions (figure 2). The crystal structure is further stabilized by the π - π stacking interactions between pyridyl rings along b-axis shown in figure 3. The list of bond lengths and bond angles are presented in the table 2.

3.2 IR spectrum of **1**

As shown in figure 4, strong and broad absorption bands in the range of 3200 to 3600 cm^{-1} in the IR spectrum are assigned to the characteristic peaks of O-H and hydrogen bonded O-H vibrations.²¹ The weak absorption peaks appeared at 1606, 1589 and 1485 cm^{-1} correspond to C=C stretching vibrations of the aromatic group. The absence of absorption bands in the range 1690-1760 cm^{-1} indicates deprotonation of the ligand. The absorption peak at 1264 cm^{-1} corresponds to C-O stretching vibrations of carboxylato group. The characteristic bands at 652 and 579 cm^{-1} represent the presence of M-N and M-O bonds in the crystal structure, respectively.^{22,23}

3.3 Thermal stability of **1**

In general, the lanthanide ions show high thermodynamic stability owing to a high coordination number.²⁴ As shown in figure 5, the synthesized coordination polymer exhibited remarkable thermal stability up to 450°C. Weight loss of 9.05% at 180°C in the TG curve corresponds to the loss of H₂O molecules (calculated 8.8%). The second significant weight loss of 43.05% at 550°C indicates the decomposition of 2,5-pydc ligand (calculated 43.40%). Similar results were substantiated by the DTA curve of the complex. Two representative endothermic peaks were observed in the DTA curve. The first endotherm at about 180°C is postulated to be

Table 2. Selected bond lengths (Å) and angles (°) for coordination polymer **1**.

Sm1-O2	2.423(6)	O2—Sm1—O5	105.4(2)
Sm1-O5	2.483(7)	O2—Sm1—O6	115.9(2)
Sm1-O6	2.656(6)	O2—Sm1—O7	75.5(2)
Sm1-O7	2.496(6)	O2—Sm1—N1	63.1(2)
Sm1-N1	2.613(8)	O5—Sm1—O6	136.2(2)
Sm1-O6	2.361(6)	O5—Sm1—N1	71.1(3)
Sm1-O1	2.422(7)	O5—Sm1—O1	71.8(2)
Sm1-O3	2.420(7)	O6—Sm1—O7	50.1(2)
Sm1-O4	2.435(7)	O6—Sm1—N1	114.9(2)
		O6—Sm1—O1	133.8(2)
		O7—Sm1—N1	70.9(2)
		O3—Sm1—N1	135.8(2)
		O4—Sm1—N1	77.2(2)
		O1—Sm1—O3	71.7(2)
		O1—Sm1—O4	138.7(2)

Symmetry codes: (i) x,y,z (ii) 1/2-x,1/2+y,1/2-z (iii) -x,-y,-z (iv) 1/2+x,1/2y,1/2.

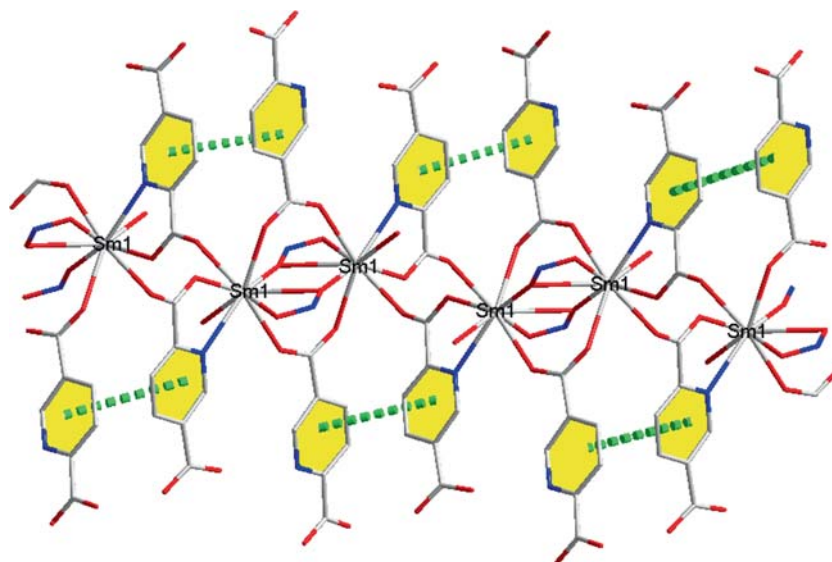


Figure 3. Perspective view of π - π stacking interactions in framework of **1**.

due to removal of water molecule from crystal structure. The second endotherm around 550°C is accorded to the decomposition of the ligand. The above said thermal results correlate with the structural features of **1**.

3.4 Luminescence properties of **1**

The solid state luminescence property of **1** along with free ligand was investigated at room temperature. On photoexcitation at 365 nm, a characteristic peak at 583 nm was observed in the emission spectrum of **1** (figure 6). The yellow luminescence observed at 583 nm is possibly due to $^4G_{5/2}$ to $^6H_{7/2}$ transition. The aforesaid observation is supported by the previous reports on lanthanide complexes with aromatic pyridine

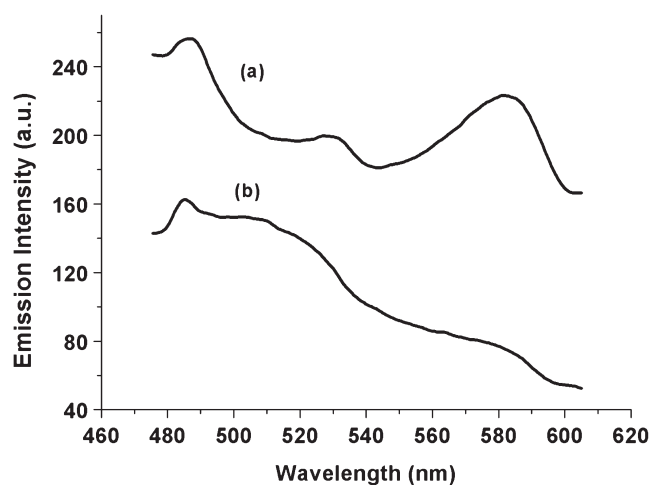


Figure 6. Photoluminescence spectra of (a) complex **1**, and (b) free ligand.

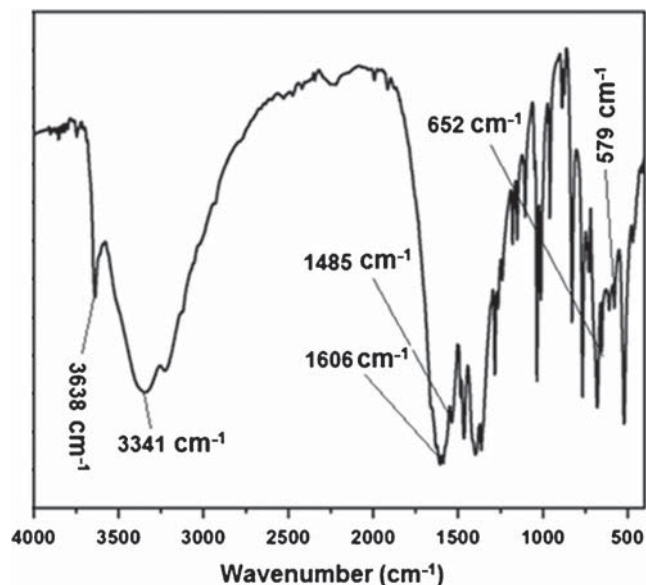


Figure 4. FT-IR spectrum of **1**.

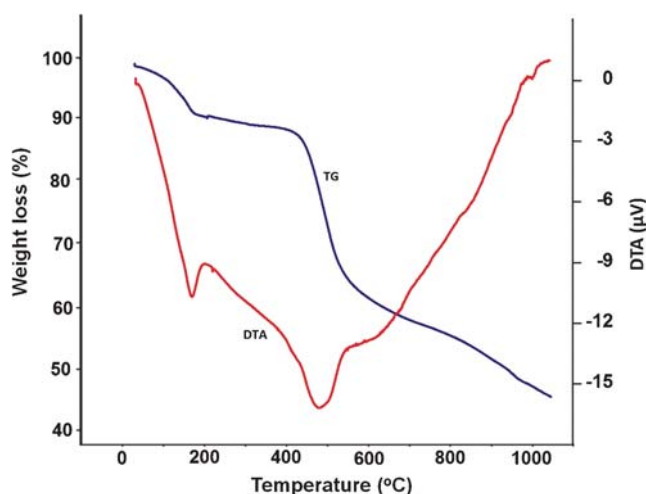


Figure 5. TG-DTA curves of **1**.

carboxylic acids where most of the emission was reported to lie between 495 and 650 nm for Sm(III), Tb(III), Dy(III) and Eu(III).^{25–27} The weak intensity of the absorption bands may be attributed to the transfer of insufficient energy from ligand to Sm(III) ions and also to the presence of coordinated water molecules minimizing the luminescence intensity of rare earth ions.²⁸

4. Conclusions

In summary, coordination polymer [Sm(2,5-pydc)(NO₃)(H₂O)].H₂O (**1**) had been synthesized by hydrothermal reaction of Sm(NO₃)₃·6H₂O and 2,5-pydcH₂ in water-acetonitrile medium. Sm(III) exhibits monocapped square antiprismatic geometry in this coordination polymer. The bridging of the two Sm(III) ions through oxygen atoms of nitrate group results in dinuclear units. Further, 2,5-pydc ligands connect with these dinuclear units to give rise to a three dimensional coordination network. The π - π interactions between pyridyl rings stabilize this architecture. The synthesized Sm(III) coordination polymer acts as a potential yellow light emitter.

Supplementary Information

CCDC 998830 contains the supplementary crystallographic data for coordination polymer **1**. 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: deposit@ccdc.cam.ac.uk. cif and Check-cif files are available at www.ias.ac.in/chemsci.

Acknowledgements

We thank Dr. Abhijit Saha, UGC-DAE Consortium for Scientific Research, Kolkata Centre, India for assisting in PL measurements.

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