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Synthesis, Structure, and Fluorescence of a Novel Samarium Compound[1]

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Abstract—A novel samarium compound, $[Sm(Phen)_2(H_2O)_5]_2(Phen)_2(Bipy)Cl_6 \cdot 7H_2O$ (**I**) (Phen = 1,10-phenanthroline and Bipy = 2,2'-bipyridine), was prepared by a solvothermal reaction. The crystal structure of **I** was characterized by X-ray single-crystal diffraction method (CIF file CCDC no. 1025736). Compound **I** is an isolated structure with the samarium ions possessing a nine-coordinated distorted mono-capped square antiprism geometry. There are abundant hydrogen bonding and π–π stacking interactions which connect the molecules together to yield a three-dimensional (3D) supramolecular structure. The fluorescence spectra data reveals that **I** can display the characteristic emission $^4G_{5/2} \rightarrow {}^6H_J$ transitions (J = 5/2, 7/2, 9/2 and 11/2, respectively) of Sm^{3+} ions.

Keywords: samarium complex, crystal structure, fluorescence, 1,10-phenanthroline

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INTRODUCTION

Lanthanide elements and their compounds have a lot of applications because of their rich properties, such as electronic polishers, optoelectronics, catalysts, hybrid car batteries, photoluminescence, optical fiber and magnetism [1]. Nowadays, a great number of lanthanide compounds with different ligands have been reported [2, 3]. N-containing ligands such as 1,10-phenanthroline [4], 2,2'-bipyridine [5], imidazole [6], isonicotinic acid [7], 4,4'-bipyridine [8] and nicotinic acid [9] are useful and widely applied to synthesize compounds [10, 11]. We report herein the preparation, structure and fluorescence of a novel samarium compound $[Sm(Phen)_2(H_2O)_5]_2$-$(Phen)_2(Bipy)Cl_6 \cdot 7H_2O$ (**I**), where Phen = 1,10-phenanthroline and Bipy = 2,2'-bipyridine), which was obtained via a solvothermal reaction.

EXPERIMENTAL

All reagents and chemicals were of analytical grade, used as commercially purchased and without further purification. The fluorescence was measured on a JY FluoroMax-3 spectrometer.

Synthesis of I. An aqueous solution (7 mL) containing $SmCl_3 \cdot 6H_2O$ (0.2 mmol, 73 mg), Phen (1.0 mmol, 180 mg), Bipy (0.2 mmol, 31 mg) and 3 mL ethanol was placed in a Teflon-lined stainless-steel vessel (25 mL) under autogenously pressure, which was heated to 180°C for 5 days, then cooled down to room temperature and colorless block crystals were obtained.

X-ray structural determination. A single crystal with dimensions of 0.15 × 0.14 × 0.07 mm was mounted on a glass fiber and the data set was collected on a Rigaku Mercury CCD X-ray area-detector diffractometer equipped with a MoK_α radiation (λ = 0.71073 Å) at 296(2) K by using an ω scan mode. Absorption corrections were applied by using CrystalClear software. The structure was solved by direct methods and refined with full-matrix least-squares technique using the Siemens SHELXTL™ Version 5 package software [12]. Anisotropic thermal parameters were applied to the non-H atoms, while the H-atoms were assigned with isotropic factors. Important crystallographic data is given in Table 1. The selected bond distances and bond angles are shown in Table 2.

Crystallographic data for structure **I** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication (CCDC no. 1025736; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The crystallographically independent unit of the title compound is comprised of two $Sm(Phen)_2(H_2O)_5$ moieties, two Phen molecules, one Bipy molecule, six

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[1] The article is published in the original.

Table 1. Crystallographic data and structure refinement for complex **I**

Parameter	Value
Formula	$C_{82}H_{90}N_{14}O_{17}Cl_6Sm_2$
Formula weight	2057.08
Color	Colorless
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	10.3923(6)
b, Å	12.9456(7)
c, Å	17.3666(9)
α, deg	74.9960(10)
β, deg	81.8960(10)
γ, deg	79.8260(10)
V, Å^3	2210.1(2)
d_{calcd}, g/cm^3	1.546
Z	1
F(000)	1042
μ, mm^{-1}	1.570
$2\theta_{max}$, deg	50
Index ranges	$-12 \le h \le 12$, $-15 \le k \le 15$, $-19 \le l \le 20$
Reflections collected	13239
Independent/observed reflections (R_{int})	12447/10956 (0.0163)
T, K	296(2)
R_1, wR_2	0.0464, 0.1097
S	1.047
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	0.860/–1.596

chloride ions and seven lattice water molecules (Fig. 1). The samarium ions are coordinated by five oxygen atoms of five coordinating water molecules and four nitrogen atoms of two Phen ligands to yield a nine-coordinated distorted monocapped square antiprism geometry. To our knowledge, the title compound is the first example of samarium compounds with Phen and Bipy molecules.

The bond distances of Sm–O are between 2.3739(8) and 2.4987(9) Å, which are normal and comparable with those found in the literature [13–16]. The bond lengths of Sm–N are in the range of 2.5801(8)–2.7486(9) Å, which are also in the normal range and comparable with the values reported in the references [17–20]. The dihedral angle between the pyridyl rings of the Bipy molecule is 1.80°. The deviation of the atoms on the Phen is between –0.179 and +0.107 Å, apart from their mean ring plane. There are many hydrogen bonding and π–π stacking interactions existing in the title compound, as the dashed lines showing in Fig. 2. These hydrogen bonding and π–π stacking interactions connect the molecules together to form a 3D supramolecular structure (Fig. 2).

Table 2. Selected bond distances (Å) and bond angles (deg)

Bond	d, Å	Bond	d, Å
Sm(1)–O(1w)	2.4300(7)	Sm(2)–O(6w)	2.4711(7)
Sm(1)–O(2w)	2.4486(11)	Sm(2)–O(7w)	2.4100(8)
Sm(1)–O(3w)	2.4955(8)	Sm(2)–O(8w)	2.4767(10)
Sm(1)–O(4w)	2.4166(9)	Sm(2)–O(9w)	2.4987(9)
Sm(1)–O(5w)	2.4194(9)	Sm(2)–O(10w)	2.3739(8)
Sm(1)–N(1)	2.6422(9)	Sm(2)–N(5)	2.7368(10)
Sm(1)–N(2)	2.6720(8)	Sm(2)–N(6)	2.7025(9)
Sm(1)–N(3)	2.5801(8)	Sm(2)–N(7)	2.6989(9)
Sm(1)–N(4)	2.7486(9)	Sm(2)–N(8)	2.7199(8)
Angle	**ω, deg**	**Angle**	**ω, deg**
N(1)Sm(1)N(2)	61.92(3)	N(5)Sm(2)N(6)	60.23(3)
N(1)Sm(1)N(3)	143.06(3)	N(5)Sm(2)N(7)	130.09(3)
N(1)Sm(1)N(4)	129.53(3)	N(5)Sm(2)N(8)	133.06(3)
N(2)Sm(1)N(3)	144.46(3)	N(6)Sm(2)N(7)	145.70(3)
N(2)Sm(1)N(4)	130.08(3)	N(6)Sm(2)N(8)	142.88(3)
N(3)Sm(1)N(4)	61.55(3)	N(7)Sm(2)N(8)	60.15(3)

It is well-known that the samarium is an excellent fluorescence active element and, therefore, we believe that the title compound should display fluorescent property. In order to confirm this, we measured the fluorescent spectra of **I** with solid state samples under room temperature (Fig. 3). The excitation spectrum of **I** has a maximum value at 368 nm. The emission spectrum of **I** shows a band at 443 nm, which is probably a ligand-based emission. Besides this band, there are four emission bands locating at 564, 598 (with a splitting band of 606 nm), 642 and 705 nm. They are originated from the *f–f* transitions of the 4*f* electrons of the Sm^{3+} ions, which can be assigned to the characteristic emission $^4G_{5/2} \rightarrow {^6H_J}$ transitions (J = 5/2, 7/2, 9/2 and 11/2, respectively) of the Sm^{3+} ions.

Thus, a novel samarium compound has been synthesized through a solvothermal reaction. It is characterized by an isolated structure with the samarium ions possessing a nine-coordinated distorted monocapped square antiprism geometry. The abundant hydrogen bonding and π–π stacking interactions link the molecules together to construct a 3D supramolecular structure.

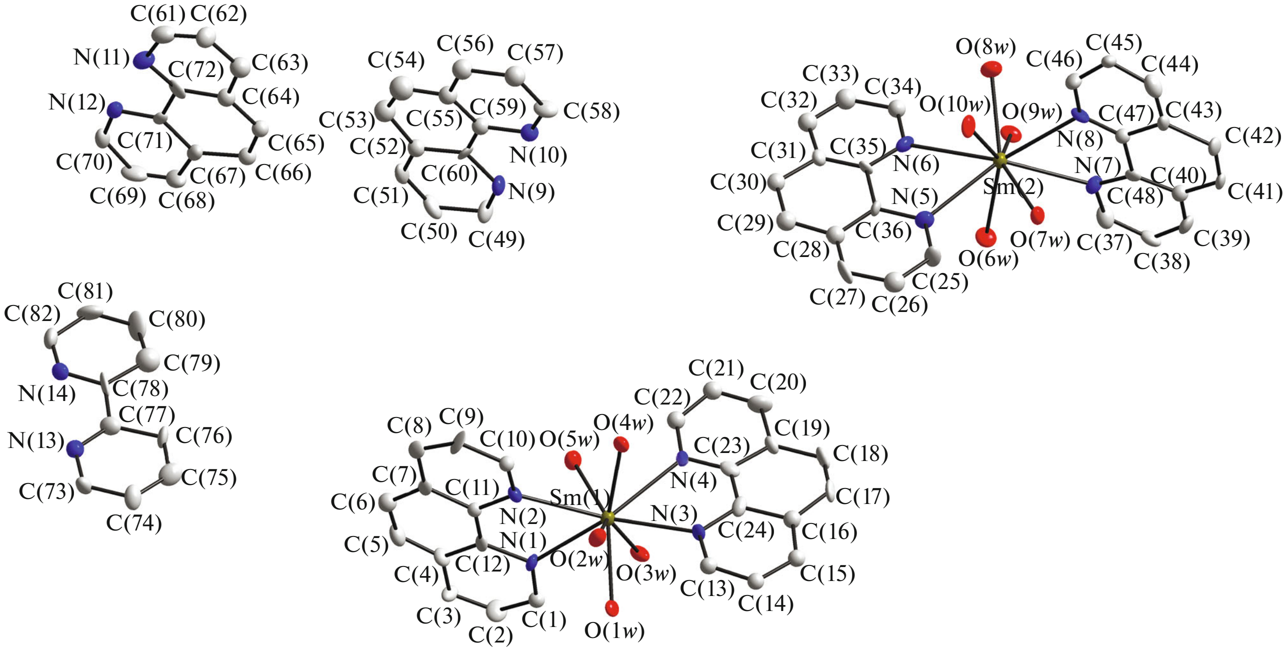

Fig. 1. ORTEP view of **I** in 25% ellipsoid probability with the chloride ions, lattice water molecules and hydrogen atoms been omitted for clarity.

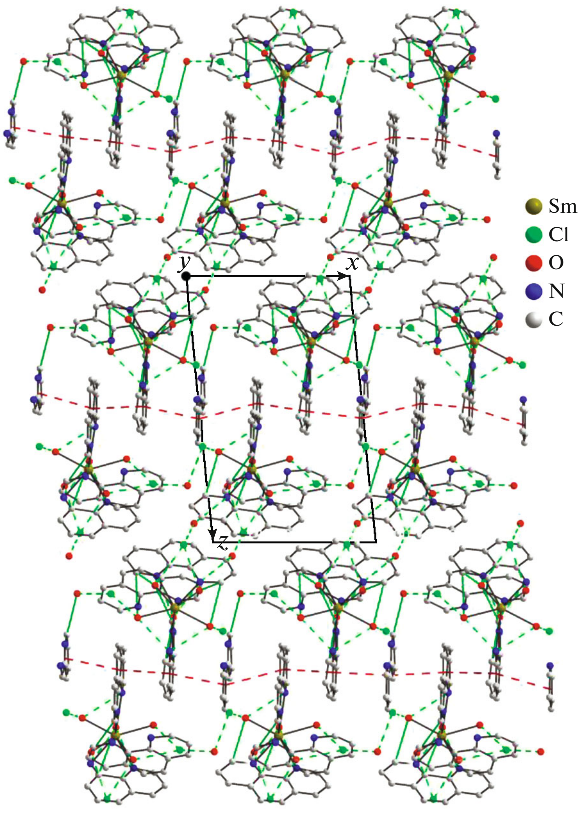

Fig. 2. A packing diagram of **I** with dashed lines representing hydrogen bonding and π–π stacking interactions, respectively (Å): O(1*w*)–H(1*wA*)···Cl(2) 3.1796(8), O(2*w*)–H(2*wA*)···Cl(2) 3.2540(10), O(4*w*)–H(4*wA*)···Cl(5) 3.0207(10), O(5*w*)–H(5*wA*)···N(9) 2.9935(13), O(6*w*)–H(6*wA*)···Cl(6) 3.0668(10), O(7*w*)–H(7*wA*)···N(11) 2.9229(13), O(8*w*)–H(8*wA*)···Cl(3) 3.2067(11), O(9*w*)–H(9*wA*)···Cl(3) 3.0800(9), C(73)–H(73*A*)···O(11*w*) 3.1701(12), C(76)–H(76*A*)···O(10*w*) (1 + *x*, *y*, *z*) 2.7833(8). Cg2···Cg10 3.6031(7), Cg3···Cg13 3.7170(6), Cg4···Cg14 3.7676(6), Cg5···Cg13 (–1 + *x*, *y*, *z*) 3.6794(6), Cg6···Cg14 (–1 + *x*, *y*, *z*) 3.5782(5), Cg7···Cg12 3.5889(8), Cg9···Cg15 3.6802(7), Cg14···Cg16 3.7554(6), Cg16···Cg6 3.8792(7), Cg17···Cg13 (–1 + *x*, *y*, *z*) 3.7683(6), Cg18···Cg11 3.6648(8) [Cg2–Cg7 and Cg9–Cg18 stand for the centers of gravity of the rings N(2)(C(7)–C(11)), N(3)(C(13)–C(16), C(24)), N(4)(C(19)–C(23)), N(5)(C(25)–C(28), C(36)), N(6)C((31)–C(35)), N(7)(C(37)–C(40), C(48)), N(9)(C(49)–C(52), C(60)), N(10)(C(55)–C(59)), N(11)(C(61)–C(64), C(72)), N(12)(C(67)–C(71)), N(13)(C(73)–C(77)), N(14)(C(78)–C(82)), (C(4)–C(7), C(11), C(12)), (C(16)–C(19), C(23), C(24)), (C(28)–C(31), C(35), C(36)), (C(40)–C(43), C(47), C(48)), respectively].

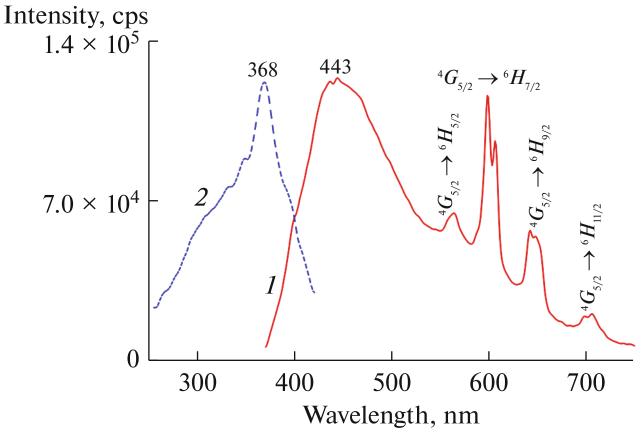

Fig. 3. Solid-state emission (*1*) and excitation (*2*) spectra of **I** at room temperature.

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