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Structure and luminescent property of a Sm^{3+} complex containing benzoyltrifluoroacetone and 1,2-bis[(anthracen-9-ylmethyl)amino]ethane ligands

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Abstract:

One of the rare earth coordination compounds that has been studied the most in-depth is -diketonate complexes. This is mostly because they can be rapidly synthesized, are sold commercially, and have a wide range of uses, including photoluminescence and magnetism. The narrow and strong emission of rare earth ions with P-diketonates makes them applicable in optical and electroluminescent devices as well as in luminescence sensors for cations and anions. The synthesis, structure, and luminescent properties of a samarium(III) complex (A2) containing benzoyltrifluoroacetone (HTFPB) and 1,2-bis[(anthracen-9-ylmethyl) amino]ethane (BAAE2) ligands are herein reported. The structure of A2 has been elucidated by infrared spectroscopy and single crystal X-ray diffraction. X-ray crystallographic analysis demonstrated that A2 has a mononuclear structure with a formula of $Sm(TFPB)_3(BAAE2)$ in which Sm^{3+} ion is coordinated to six O-atoms from three TFPB ligands and two N-atoms from one ancillary ligand (BAAE2). The substantial absorptions generated by the -diketonate and anthracenyl fragments are confirmed by UV-Vis measurements. The data show that A2 strongly absorbs in the region of 220-400 nm. Nonetheless, A2 gives poor emission due to a quenching effect of the anthracenyl moiety.

Keywords: **anthracene, β-diketone, rare earth complex.**

Classification number: **2.2**

1. Introduction

β-diketonate complexes are among the most thoroughly explored rare earth coordination compounds. This is mainly due to the fact that they are easily synthesized, readily available from commercial sources, and are utilized in many applications ranging from magnetism to photoluminescence [1, 2]. The narrow and strong emission of rare earth ions with β-diketonates makes them applicable in optical and electroluminescent devices as well as in luminescence sensors for cations and anions. However, due to "Laporte-forbidden" f-f transitions, emissions from the direct excitation of lanthanide ions are infeasible [3]. Benzoyltrifluoroacetone (HTFPB) is a commercially available and efficient sensitizer that is able to transfer excited energy to rare earth ions. Due to the suitable triplet energy level of TFPB, a so-called "antenna effect" is produced that turns on lanthanide emissions. Typically, the synthesis of lanthanide β-diketonates in the first step involves two water molecules in the coordination sphere of the central metal ion. Subsequent displacement of the coordinated water by ancillary chelating ligands with various electronic structures may lead to a fine tuning of lanthanide-centered emissions [4-6]. It has been well documented that bispyridine, phenanthroline, and many pyridine-based ligands are able to turn on the emission of the central metal ion due to additional sensitizer effects [7, 8]. In this study, 1,2-bis[(anthracen-9-ylmethyl)amino]ethane (BAAE2), a ligand with a low-lying triplet state, has been utilized to construct a tris β-diketonate complex [9-12]. BAAE2 is a potentially good bidentate ligand as the trivalent rare-earth ions are Lewis acids that preferentially form complexes with nitrogen donor bases. In the following discussions, the main attention will be focused on the syntheses, structures, and luminescent properties of Sm^{3+} complexes containing TFPB and BAAE2 ligands.

2. Experimental

2.1. Synthesis of ligands and complexes

2.1.1. Synthesis of BAAE2 ligand

Step 1: Synthesis of BAAE1 [13]

BAAE1 was synthesized via a condensation reaction between ethylenediamine and anthracene-9-carcbadehyde, which is depicted in Scheme 1.

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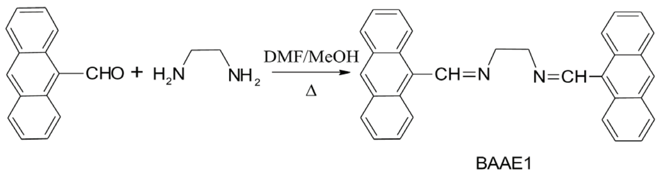
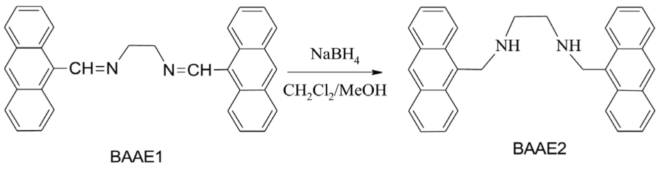


Scheme 1.

A solution of anthracene-9-caboxaldehyde (0.400 g; 1.94 mmol) in 12 ml DMF/CH_3OH (v/v, 1:5) was added to ethylenediamine (0.067ml, 0.97 mmol) in methanol and the mixture was refluxed for 4 h with constant stirring. After the solution had cooled to room temperature, a yellow precipitate was formed and collected by vacuum filtration. The product was washed by a few drops of DMF, a large amount of methanol, and air-dried. The yield was 0.364 g (86%).

Step 2: Synthesis of BAAE2 ligand [13]

The synthetic procedure of ligand BAAE2 was based on a reaction reducing ligand BAAE1 by $NaBH_4$ in methanol as described in Scheme 2.



Scheme 2.

BAAE1 (0.396 g, 0.907 mmol) was dissolved in a mixture of CH_2Cl_2 (30 ml) and CH_3OH (15 ml) to obtain a yellow solution. A solution of $NaBH_4$ (0.527 g, 13.9 mmol) in methanol (3 ml) was added under stirring to the mixture. The solution was stirred overnight at room temperature to give a yellow solid. The product was washed several times with distilled water, finally with diethyl ether, and air-dried. The yield was 0.320 g (80%).

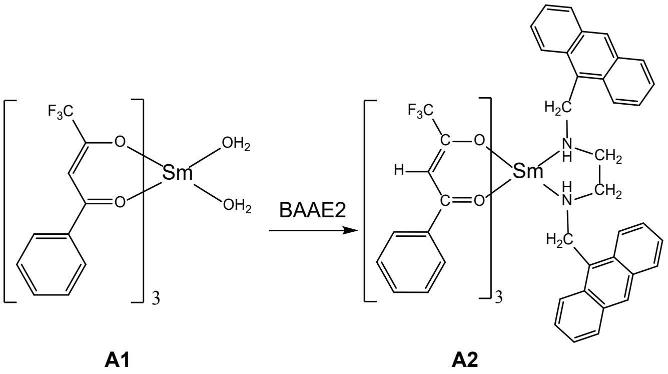
2.1.2. Synthesis of the complexes

Synthesis of $Sm(TFPB)_3(H_2O)_2$ complex (**A1**)

Sm_2O_3 (0.070 g, 0.2 mmol) was dissolved in HCl at 50°C, then distilled water was added and heated at 100°C to form $SmCl_3$. A solution of NaOH (0.048 g, 1.2 mmol) and HTFPB (0.259 g, 1.2 mmol) in MeOH (15 ml) was added dropwise under stirring to a solution of $SmCl_3$ in MeOH (15 ml). The mixture was stirred at room temperature until a white solid completely formed. The product was washed by a large amount of CCl_4 and air-dried. The yield was 88%.

Synthesis of $Sm(TFPB)_3$BAAE2 complex (**A2**)

A2 was achieved by reacting **A1** with BAAE2 ligand in chloroform-methanol solvent mixture (Scheme 3).



Scheme 3.

A solution of BAAE2 (0.397 g, 1 mmol) in $CHCl_3$ (15 ml) was added dropwise under stirring to a solution of **A1** (0.831 g, 1 mmol) in MeOH (15 ml). The mixture was stirred at room temperature for about 1 h until a yellowish precipitate formed. The solvent was removed in vacuum and the resulting solid was then washed with n-hexane. After drying under vacuum, a pale-yellow powder was obtained. The product was crystallized in EtOH/CH_2Cl_2 (v/v, 1:1) and the yield was 74%.

2.2. Measurements

The IR spectra of A2 was measured with a FT-IR 8700 infrared spectrophotometer (4000-400 cm^{-1}) in KBr pellets at Institute of Chemistry, Vietnam Academy of Science and Technology, Hanoi, Vietnam.

Single crystal X-ray diffraction data of the complex **A2** was collected on the X-ray diffractometer (Bruker D8 Quest) at 298 K at the Faculty of Chemistry, University of Science, Vietnam National University - Hanoi, Vietnam. Structure solution and refinement were performed with OLEX2 programs.

Absorption spectra of the ligands and the complexes were measured in dichloromethane at room temperature on Cary 5000 UV/Vis spectrometer at Faculty of Environmental Chemistry, Hanoi National University of Education. Emission spectra of the complexes were measured on Hitachi Fluorescence Spectrophotometer F-7000.

3. Results and discussion

3.1. Infrared spectroscopy

The infrared spectrum of the complex $Sm(TFPB)_3$BAAE2 (**A2**) is shown in Fig. 1. Typical absorption bands of the complexes and ligand are shown in Table 1.

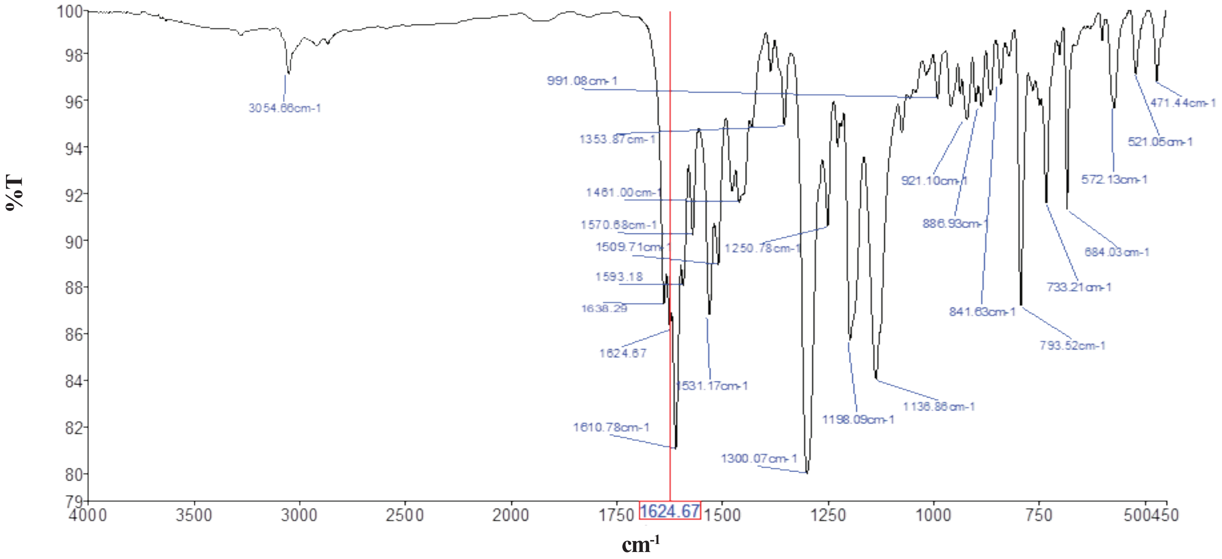


Fig. 1. The infrared spectrum of A2.

Table 1. Typical absorption bands of the complexes and ligand (cm^{-1}).

Compounds	ν_{O-H}	$\nu_{C-Caroma}$	ν_{C-F}	$\nu_{C=O}$	ν_{C-N}	ν_{Sm-O}
HTFPB	3450	3030	1191	1600	-	-
BAAE2	-	3040	-	-	1100	-
A1	3300	3035	1170	1608	-	557
A2	-	3054	1295	1609	991	562

The IR spectrum of **A1** exhibits the typical broad absorption in the region 3000-3500 cm^{-1}, which proposes the presence of water molecules coordinated to the central ion Sm^{3+}. In contrast, the absence of the broad bands in the region of 3000-3500 cm^{-1} for **A2** suggests that water molecules in **A1** have been displaced by the nitrogen donor of BAAE2 ligand. The respective ν_{C-F} vibration of **A2** is found at 1295 cm^{-1} that, compared to the starting material, is shifted to a somewhat higher frequency. The absorption at 1600 cm^{-1}, which is typical for C=O sketch in the HTFPB ligand, is red-shifted to 1609 cm^{-1} in **A2** [2]. In addition, the absorption band responsible for ν_{Sm-N} at 506 cm^{-1} in **A2** confirms the complexation of Sm^{3+} ions with BAAE2 ligands through nitrogen atoms. The change in absorption frequency of $\nu_{C=O}$ compared with free ligands and the emergence of ν_{Sm-N} absorption in the low frequency prove that HTFPB and BAAE2 ligands are present in the coordination sphere of Sm^{3+}.

3.2. Single crystal X-ray diffraction

The structure of **A2** was determined by single crystal X-ray diffraction (Fig. 2). Selected bond lengths and angles are provided in Table 2. Crystal data and data collection parameters for the complex are given in Table 3.

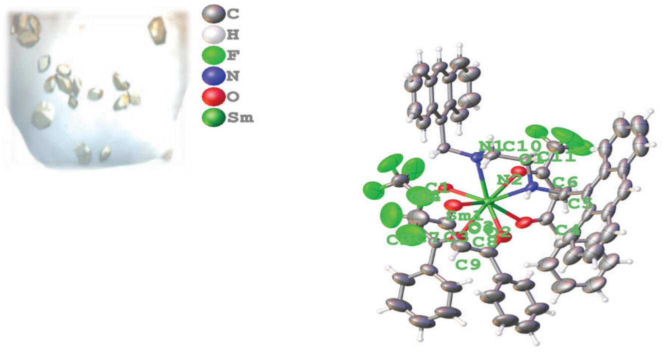


Fig. 2. Molecular structure of A2.

The structure of the complex reveals a coordination number of eight in the central metal ion in which Sm^{3+} is bonded to six oxygen atoms from three TFPB and two nitrogen atoms from the BAAE2 ligand. The bond lengths of Sm1-O are 2.355-2.418 Å. The bond lengths of Sm^{3+} with two nitrogen atoms of BAAE2 are 2.599-2.658 Å. The O-Sm1-O bond angles are nearly the same and in the range of 69.58-70.7°, which is longer than that of N-Sm1-N (67.26°). The C-N bond lengths (1.465-1.491 Å) in the complex were found to be longer than a C-N single bond (1.472 Å). This confirms the delocalization of π electrons in the chelate ring upon complexation of BAAE2. The C-C bond length in the diketonate of C2 is 1.359-1.430 Å, which is shorter than the C-C bond length (1.54 Å) but longer than that of C=C (1.34 Å). Similarly, the C-O bond length in the diketone of **A2** is 1.247-1.268 Å and it is also shorter than the bond length of C-O but longer than that of C=O. This confirms the delocalization of π electrons in the β-diketonate upon complexation between Sm^{3+} and TFPB ligands. The coordination of Sm^{3+} with BAAE2 ligands through two nitrogen atoms forms a five-membered chelate ring.

Table 2. Selected bond lengths and angles for A2.

Bond lengths/Å			
Sm1-O1	2.418(5)	O6-C14	1.249(8)
Sm1-O2	2.355(5)	N1-C1	1.491(9)
Sm1-O3	2.370(5)	N1-C2	1.465(9)
Sm1-O4	2.368(5)	N2-C3	1.486(7)
Sm1-O5	2.374(5)	N2-C4	1.478(8)
Sm1-O6	2.357(5)	N2-C5	1.480(8)
Sm1-N1	2.599(6)	C2-C3	1.351(12)
Sm1-N2	2.658(6)	C6-C7	1.394(12)
O1-C6	1.259(9)	C7-C8	1.373(12)
O2-C8	1.273(9)	C9-C10	1.418(11)
O3-C9	1.258(9)	C10-C11	1.365(10)
O4-C11	1.247(7)	C12-C13	1.496(10)
O5-C12	1.268(7)	C13-C14	1.412(10)
Bond angles/°			
O1-Sm1-O2	69.58(18)		
O3-Sm1-O4	70.7(2)		
O5-Sm1-O6	70.34(17)		
N1-Sm1-N2	67.26(17)		
C1-N1-C2	112.6(5)		
N1-C2-C3	110.4(5)		
C2-C3-N2	111.9(5)		
C3-N2-C4	109.4(5)		
C4-N2-C5	107.5(5)		
C5-N2-C3	108.9(5)		

Table 3. Crystal data and structure refinement for A2.

Formula	$C_{50}H_{50}N_6O_6F_9Sm$
M_w/g.mol^{-1}	1046.12
Crystal system	monoclinic
a/Å	10.7101(10)
b/Å	23.075(2)
c/Å	23.458(2)
α/°	90
β/°	102.355(3)
γ/°	90
Volume/Å^3	5663.0(9)
Space group	$P2_1/c$
Z	4
ρ_{calc}g/cm^3	1.227
μ/mm^{-1}	1.107
Reflections collected	33163
Independent reflections	10312 [R_{int}=0.1464, R_{sigma}=0.1418]
Data/restraints/parameters	10312/741/721
R1/wR2 [I≥2σ (I)]	R_1=0.0641, wR_2=0.1364
GOF	0.996

3.3. UV-Vis absorption spectroscopy

To determine the photophysical properties of the compounds, we measured absorption spectra of ligands and Sm^{3+} complexes in the region of 200-800 nm in a CH_2Cl_2 solvent. The absorption spectra of **A1**, **A2**, HTFPB, and BAAE2 are displayed in Fig. 3.

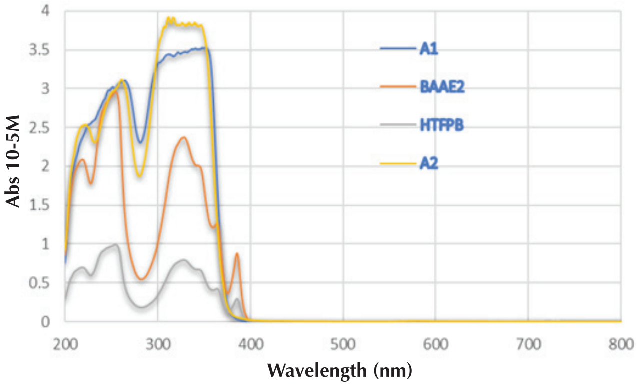


Fig. 3. Absorption spectra of A1, A2, HTFPB, and BAAE2 in CH_2Cl_2 at room temperature.

The spectra highlight strong absorptions in the region of 220-400 nm for the HTFPB and BAAE2 ligands as well as the **A1** and **A2** complexes. The broad bands observed at 327 and 328 nm are assigned to singlet-singlet π-π* transition in β-diketonate moiety [14]. These absorption bands are shifted slightly to the longer wavelength region compared with that of free HTFPB (325 nm), which hints at the perturbation of Sm^{3+} upon complexation [7]. The bands at a lower wavelength around 260 nm are anthracene-based π-π* electronic transitions. The auxiliary ligand BAAE2 is also absorbed at ultraviolet wavelengths. The lanthanide f-f transitions are not allowed, which makes absorption due to Sm^{3+} ions imperceptible in the spectra of **A1** and **A2**.

3.4. Photoluminescence spectroscopy

The photoluminescence spectra of **A1** and **A2** were studied using an excitation wavelength of 365 nm. The emission spectra are shown in the Fig. 4. Despite the quenching effect of O-H stretches, **A1** gives a strong orange color and narrow band emission. This might be due to the very efficient sensitization of TFPB to Sm^{3+}. Meanwhile, **A2** is much less emissive than **A1** but gives the same pattern of emission bands. We assume that the low-lying triplet energy level of the anthracenyl core in BAAE2 leads to intramolecular energy transfer from excited Sm^{3+}. The emission lines at 565, 603, 651, and 710 nm are assigned to the $^4G_{5/2}\rightarrow 6F_J$ (J=1/2-9/2) transitions of Sm^{3+}. The strongest emission band centered at 651 nm stems from the $^4G_{5/2}\rightarrow{}^6F_{7/2}$ transition.

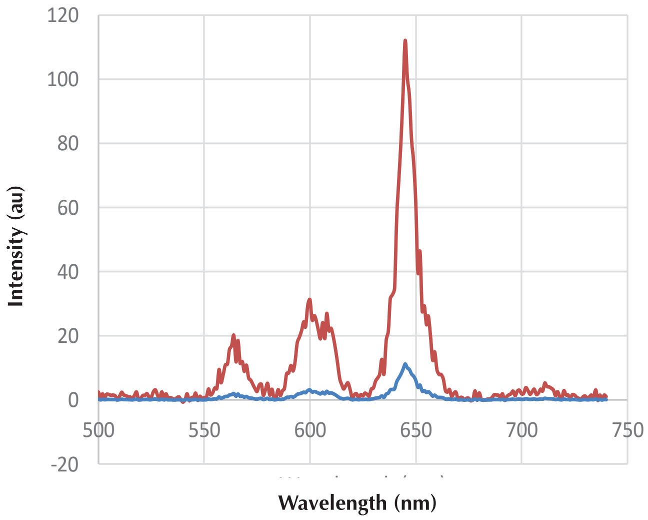


Fig. 4. PL spectra of A1 (a red line), A2 (a blue line) complexes.

4. Conclusions

Samarium (III) complexes containing TFPB and BAAE2 ligands were synthesized. The structure of **A2** was definitively determined by X-ray diffraction and revealed a five-membered chelate ring of BAAE2 with Sm^{3+} ions. The results also described that Sm^{3+} in **A2** adopts a coordination number of eight as it is bonded to six oxygen atoms from three TFPB ligands and two nitrogen atoms of BAAE2. UV-Vis results confirm the strong absorptions produced by the β-diketonate and anthracenyl fragments. The **A1** and **A2** complexes both display Sm^{3+}-centered orange emissions in which that of **A2** is much weaker due to triplet-triplet energy transfer arising from the anthracenyl ring of BAAE2. Attempts to disrupt the aromaticity of the anthracenyl ring in order to switch on Sm^{3+} emissions in **A2** are presently being made in our laboratory.

CRediT author statement

Thi Hien Dinh, Minh Hai Nguyen: Conceptualisation, Methodology, Software, Resources, Writing - Review and Editing, Validation.

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COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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