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Synthesis, Photoluminescent, and Magnetic Properties of Two Lanthanide Sulfosalicylate Complexes

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Synthesis, Photoluminescent, and Magnetic Properties of Two Lanthanide Sulfosalicylate Complexes

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Self-assembly reactions of 5-sulfosalicylic acid (ssa) and lanthanide oxides under hydrothermal condition gave rise to two hybrid polymeric complexes, namely $[Nd(ssa)(H_2O)]_n$ (1) and $\{[Tb(ssa)(H_2O)_2] \cdot H_2O\}_n$ (2). X-ray diffraction analyses reveal that complex 1 holds a three-dimensional framework and complex 2 possesses a two-dimensional network with the asymmetric unit comprising one Tb(III) ion, one sulfosalicylate ligand, and two coordinated and one free water molecule. The Fourier transform infrared spectra, thermogravimetric analyses, magnetic susceptibility, and fluorescent measurements for the complexes have been performed.

Supplemental materials are available for this article. Go to the publisher's online edition of Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry to view the supplemental file.

Keywords fluorescence, hydrothermal synthesis, lanthanide complexes, sulfosalicylate

INTRODUCTION

The significant interest in the crystal engineering of inorganic-organic hybrid materials not only results from their structurally diverse flexibility, but also from their widely promising potential applications in magnetism, photoluminescence, and catalysis.^[1–3] The lanthanides possess abundant valence-shell electronic and approximate energy-level difference (ΔE) of inner-shell 4f electrons, resulting in unique physical-chemical properties. So lanthanide complexes have been praised as a treasury of new functional materials in many fields such as fluorescence, electronic, magnetic, and catalysis.^[4–6]

In past decades, the applications of some inorganic-organic hybrid fluorescence materials have encountered great challenges in optical devices because of poor compatibility and thermal stability. This spurred scientists up to investigation into new hybrid materials. In the 40 years early, the fine behaviors of lightinduced luminescence for some Ln-organic complexes have been observed, which has attracted great interest for materials scientists.^[7,8] Presently, the commercial application of the lanthanide-organic complexes is limited by weak fluorescence properties, in which the special fluorescence enhancement might be produced by tuning lanthanide organic electronic interactions with suitable organic groups. Wherefore, selecting suitable organic ligands with special functional groups may result in a good way to assemble new functional materials. Now, the contents of the lanthanide-coordinated chemistry are extended from solution into solid state and a great number of complexes have been synthesized.^[9-13]

In this paper, we report the synthesis and structural characterizations, and magnetic and fluorescent properties of two lanthanide-sulfosalicylate hybrid polymers, $[Nd(ssa)(H_2O)]_n$ (1) and $\{[Tb(ssa)(H_2O)_2] \cdot H_2O\}_n$ (2). Complex 1 is a threedimensional framework and has been briefly reported by Wang.^[14] Complex 2 possesses two-dimensional network.

EXPERIMENTAL

Materials and Measurements

All chemicals of reagent grade were commercially available and used without further purification. Elemental analyses (C and H) were performed using a Perkin-Elmer 2400 CHNS/O analyzer (Shanghai, China). The infrared spectra of KBr pellets in the range 4000–400 cm⁻¹ were recorded on a Shimadzu 750 FTIR spectrometer (Japan). Thermogravimetric analyses were carried out from room temperature to 1000°C for 1 and 2 on preweighed samples in nitrogen stream using a Seiko Exstar6000 TG/DTA6300 apparatus with a heating rate of 10°C/min (Japan). All the excitation and emission spectra were measured with an Aminco Bowman Series 2 instrument with a xenon arc lamp as the excitation light source for the solid-state samples at room temperature (USA). Variable-temperature magnetic susceptibilities were measured using a SQUID magnetometer

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(Quantum Design Model MPMS–7, USA) in temperature range $2 \le T \le 300$ K, for polycrystalline samples of complexes 1 and 2.

Synthesis of the Complex

$[Nd(ssa)(H_2O)]_n (1)$

A mixture of Nd₂O₃ (0.067 g, 0.2 mmol), sulfosalicylic acid (0.203 g, 0.8 mmol), and water (15 mL) was placed in a 25 mL autoclave with Teflon linear and heated to 170°C for 72 h. After the reaction system was cooled to room temperature at a rate of 10°C/h, light red block-shaped crystals were isolated by filtration (yield: 30%, based on Nd₂O₃). Anal. Calcd. for C₇H₅NdO₇S, Mr = 377.41 (%): C, 22.28; H, 1.34. Found (%): C, 22.36; H, 1.29. IR (KBr, cm⁻¹): 3420(s), 3069(w), 1649(w), 1587(s), 1495(w), 1470(s), 1431(s), 1361(s), 1290(w), 1240(s), 1147(s), 1126(m), 1093(m), 1034(s), 908(w), 812(s), 756(m), 669(m), 594(s), 497(m) and 420(m).

 ${[Tb(ssa)(H_2O)_2] \cdot H_2O}_n(2)$

A mixture of Tb₄O₇ (0.075 g, 0.1 mmol), sulfosalicylic acid (0.203 g, 0.8 mmol), and water (10 mL) was placed in a 25 mL autoclave with Teflon linear and heated to 160°C for 72 h. After the reaction system was cooled to room temperature at a rate of 10°C/h, light green plate-shaped crystals were isolated by filtration (yield: 30%, based on Tb₄O₇). Anal. Calcd. for C₇H₉O₉STb, Mr = 428.12 (%): C, 19.64; H, 2.12. Found (%): C, 20.01; H, 2.14. IR (KBr, cm⁻¹): 3361(s), 1610(s), 1554(s), 1509(s), 1439(s), 1435(s), 1376(m), 1333(s), 1257(s), 1211(s), 1142(s), 1092(m), 1042(s), 914(w), 843(m), 750(w), 672(m), 598(s), 438(m).

DATA COLLECTION, STRUCTURAL DETERMINATION, AND REFINEMENT

Crystal Structure Determination

Suitable crystals of complexes 1 and 2 were carefully selected under a polarizing microscope and mounted with epoxy cement on respective fine glass fibers for single crystal X-ray

TABLE 1Crystallographic data for 1 and 2

Complex	1	2
Empirical formula	NdC7H5O7S	TbC7H9O8S
Formula weight	377.41	412.13
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal appearance	Light red block	Light green plate
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> 2(1)/n
a (Å)	6.0500(2)	8.8444(3)
b (Å)	8.2421(1)	8.8181(3)
c (Å)	9.9660(3)	14.2231(3)
α (°)	111.903(2)	90
β (°)	94.764(2)	100.688(2)
γ (°)	94.014(2)	90
$V(Å^3)$	456.74(2)	1090.03(6)
Z	2	4
D_{calc} (Mg·m ⁻³)	2.744	2.609
F(000)	358	816
Crystal size (mm)	0.40 imes 0.24 imes 0.08	$0.40 \times 0.24 \times 0.08$
Absorption coefficient (mm^{-1})	5.930	6.719
θ range for data collection (°)	2.22-25.02	2.52-25.07
Reflections collected	2410	3190
Independent reflections	1593	1895
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data $[I > 2\sigma(I)]$ /parameters	1593 / 157	1895 / 187
Goodness-of-fit on F^2	1.087	1.209
R_1 indices (I > $2\sigma(I)$)	0.0356	0.0421
wR ₂ indices (all data)	0.0943	0.997
Largest diff. peak / hole (e Å ⁻³)	1.132/-1.489	0.888/-1.644

diffraction analyses. Data collections for **1** and **2** were performed on a Siemens SMART-CCD diffractometer equipped with a graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 293 K. Empirical absorption corrections were applied using the SADABS program.^[15] The structures were solved by direct methods, the metal atoms were located from the E-map, and other non-hydrogen atoms were derived from the successive difference Fourier syntheses. The hydrogen atoms were located from the difference map and refined isotropically. The structures were refined on F^2 by full-matrix least-squares using the SHELXTL-97 program package.^[16] The crystallographic data of complexes **1** and **2** are listed in Table 1 and selected bond lengths and angles in Table 2. Additional crystallographic details and complete listings of the complexes **1** and **2** have been deposited at the Cambridge Crystallographic Data Center (CCDC 259028 for 1, 787782 for 2).

RESULTS AND DISCUSSION

Synthesis

Due to the strong affinity of lanthanide ions for oxygen and the coordination versatilities of the carboxylate/sulfonate group, the rigid multicarboxylate/sulfonate ligands are therefore selected for the construction of lanthanide coordination complexes with the desired structural features and special properties. It is well known that lots of reaction factors can affect to the formation of crystal structure, such as initial reactants, pH value, molar ratio, reaction time, and temperature in the process of

 TABLE 2

 Selected bond lengths (Å) and angles (°) for 1 and 2

1		2	
Nd-O(3)	2.400 (5)	Tb(1)-O(3)#1	2.289 (6)
Nd-O(2)#1	2.401 (5)	Tb(1)-O(4)#2	2.344 (7)
Nd-O(3)#1	2.421 (5)	Tb(1)-O(1)#1	2.349 (6)
Nd-O(7)	2.449 (5)	Tb(1)-O(6)#3	2.358 (6)
Nd-O(6)#2	2.457 (6)	Tb(1)-O(8)	2.380 (7)
Nd-O(4)#3	2.471 (5)	Tb(1)-O(7)	2.389 (7)
Nd-O(2)#4	2.472 (5)	Tb(1)-O(2)	2.414 (7)
Nd-O(1)#4	2.606 (6)	Tb(1)-O(1)	2.530 (6)
Nd-Nd#1	3.9749 (7)	Tb-Tb#1	4.506 (7)
S-O(5)	1.446 (6)	S(1)-O(5)	1.450 (7)
S-O(4)	1.459 (5)	S(1)-O(6)	1.460 (7)
S-O(6)	1.477 (6)	S(1)-O(4)	1.462 (7)
S-C(6)	1.764 (6)	S(1)-C(4)	1.758 (9)
O(3)-Nd-O(2)#1	109.80 (18)	O(3)#1-Tb(1)-O(8)	76.5 (2)
O(3)-Nd-O(3)#1	68.93 (19)	O(4)#2-Tb(1)-O(8)	74.8 (2)
O(3)-Nd-O(7)	153.84 (19)	O(1)#1-Tb(1)-O(8)	117.8 (2)
O(2)#1-Nd-O(7)	73.9 (2)	O(6)#3-Tb(1)-O(8)	140.9 (2)
O(3)#1-Nd-O(7)	133.69 (19)	O(6)#3-Tb(1)-O(7)	71.5 (2)
O(3)-Nd-O(6)#2	78.67 (19)	O(8)-Tb(1)-O(7)	142.0 (2)
O(7)-Nd-O(6)#2	103.2 (2)	O(3)#1-Tb(1)-O(2)	138.7 (2)
O(3)-Nd-O(4)#3	133.72 (18)	O(4)#2-Tb(1)-O(2)	81.1 (2)
O(7)-Nd-O(4)#3	71.4 (2)	O(1)#1-Tb(1)-O(2)	146.3 (2)
O(3)-Nd-O(2)#4	83.46 (17)	O(6)#3-Tb(1)-O(2)	106.5 (2)
O(7)-Nd-O(2)#4	74.6 (2)	O(8)-Tb(1)-O(2)	74.5 (3)
O(3)-Nd-O(1)#4	86.43 (18)	O(7)-Tb(1)-O(2)	76.8 (2)
O(7)-Nd-O(1)#4	68.7 (2)	O(3)#1-Tb(1)-O(1)	92.1 (2)
O(6)#2-Nd-O(1)#4	78.57 (18)	O(4)#2-Tb(1)-O(1)	130.7 (2)
O(4)#3-Nd-O(1)#4	128.31 (19)	O(8)-Tb(1)-O(1)	76.4 (2)
O(2)#4-Nd-O(1)#4	50.80 (16)	O(7)-Tb(1)-O(1)	104.9 (2)
O(3)#1-Nd-O(1)#4	153.93 (19)	O(2)-Tb(1)-O(1)	52.9 (2)
O(2)#1-Nd-O(1)#4	111.52 (17)	O(1)#1-Tb(1)-O(8)	117.8 (2)
Nd#1-Nd-Nd#5	96.945 (15)	Tb(1)#4-O(1)-Tb(1)	134.9 (3)

Symmetry transformations used to generate equivalent atoms. For 1: #1 - x, -y + 1, -z + 1; #2 - x, -y + 1, -z + 2; #3 x, y - 1, z - 1; #4 x + 1, y, z; #5 - x + 1, -y + 1, -z + 1. For 2: #1 - x + 3/2, y - 1/2, -z + 3/2; #2 - x + 1, -y + 1, -z + 2; #3 x + 1/2, -y + 3/2, z - 1/2.

hydrothermal syntheses. In these synthesis systems, if the lanthanide oxide replaced lanthanide nitrate (or halogen) in the reaction mixtures, only clear solution of reaction mixtures were obtained; when the pH value was raised to 5–7 for the reaction mixtures previously, only related mass precipitates were isolated, which may result from the Ln(III) ions being sensitive to the acidization of the reaction systems. When changing the reaction time, temperatures or molar ratio, the micro/polycrystals collected are not suitable for single X-ray diffraction analysis, indicating design and assembly of new lanthanide complexes remain many challenges and opportunities in terms of controlling their shapes and dimensions.

IR Spectrum

The IR spectrum of complex **2** (Figure S5, Supplementary data) exhibits a strong broad peak at 3361 cm⁻¹ for ν (O-H) vibration associated with the water molecules. The absence of the characteristic absorption peaks at 1730–1690 cm⁻¹ for **2** indicates the ssa ligands were completely deprotonated to the terbium ions. The feature at 1609 cm⁻¹ attribute to the v(COO) vibration, and the peak 1554(s) cm⁻¹ is assigned to the ν_s (C=O) vibration; 1510(vs) cm⁻¹ to the (C-C)_{skeletal}. The sulfonate group R-SO₃⁻ shows strong absorption peaks of ν (S-O) vibrations found in the region 1055–1300 cm⁻¹; the peaks of ν (C-S) are found in the region 1011–1045 cm⁻¹. The IR spectrum of complex **1** (Figure S6, Supplementary data), being similar to ones of **2**, shows a broad peak at 3420 cm⁻¹ associated with the water molecules. The characteristic absorption peak at 1649 cm⁻¹ are assigned to the carboxylate group, the characteristic

peaks at 1093 cm^{-1} and 1034 cm^{-1} attribute to the sulfonate group.

Structure Description of the Complex

$[Nd(ssa)(H_2O)]_n$ (1)

The crystallographic analysis reveals that complex 1 possesses a three-dimensional framework.^[14] The central Nd(III) ion is coordinated by eight oxygen atoms, of which two oxygen atoms come from sulfonate group, two oxygen atoms from benzene-hydroxyl oxygen groups, three oxygen atoms from carboxylates, and one oxygen atom from coordinated water molecule with Nd-O distances range from 2.400 to 2.606 Å. Each SSA ligand acts as a heptadentate connector to link five neodymium ions (Figure S1, Supplementary data), in which each deprotonated carboxylate group adopts a bidentate chelating-bridging mode connecting two neodymium ions, each benzene-hydroxyl oxygen atom as μ_2 -bridge links two neodymium ions, forming a one-dimensional chain (Figure S2). The chain is extended by bridging of the sulfonate group into two-dimensional network (Figure S3), which further grows in different direction to the final three-dimensional framework with novel microporous channels (Figure S4).

${[Tb(ssa)(H_2O)_2] \cdot H_2O}_n(2)$

Single X-ray diffraction analysis reveals that complex **2**, being similar to the lanthanide compounds reported,^[17] holds a two-dimensional network, in which the asymmetric unit consists of one Tb(III) ion, one sulfosalicylate ligand, and two coordinated water molecules and one free water molecule. In the coordination environment of **2**, the central Tb(III) ion is



FIG. 1. Linking fashion of the sulfosalicylate ligand in 2 (color figure available online).



FIG. 2. Two-dimensional network for 2 (color figure available online).

eight-coordinated, of which three oxygen atoms come from two different carboxylates, two oxygen atoms from two different sulfonates, two oxygen atoms from the coordination water molecules, and one oxygen atom from the hydroxyl group, forming a trigonal dodecahedron polyhedron that centers TbO₈ with Tb-O distances including 2.289–2.531 Å, the S-O distance of 1.45 Å, S-C distance of 1.758 Å, and Tb-Tb distance of 4.506Å. The sulfosalicylate ligand serves as μ_4 -bridge linking four Tb(III) ions (Figure 1) by a bidentate bridging mode of the sulfonate, a bidentate chelating-bridging mode of the carboxylate, and a monodentate mode of the hydroxyl group, finally resulting in two-dimensional framework (Figure 2).

Thermal Analysis

Thermogravimetric analyses (TGA) of complex 1 and 2 have been measured under a flow of nitrogen from room temperature to 1000° C at a heating rate of 10° C/min.

Differential thermal analyses of **1** show two main absorption heat peaks at 385° C and 675° C, which indicate the complex took corresponding chemical or physical reaction. The first weight loss of 4.53% (calculated: 4.77%) from about 334° C to 407° C corresponds to the loss of one coordination water molecule per formula unit [Nd(ssa)(H₂O)]_n, and then only few of the weight was lost from 407° C to 587° C. The second distinct weight loss of 27.38% (calculated: 28.50%) from 587° C to 705° C corresponds to the loss of half sulfosalicylate ligand per formula unit, which indicates that the framework of [Nd(ssa)]_n came about collapse. The final decomposed product presumably is Nd₂O₃, 60% (calculated: 64.86%, based on the framework of [Nd(ssa)]_n (Figure S7).

Differential thermal analyses (DTA) of **2** exhibit two strong absorption heat peaks at 175 and 670° C, respectively, which indicate the complex took corresponding chemical or physical reaction. The TGA curve reveals that complex **2** began to lose weight at 80°C, the weight loss of 11.71% (calculated: 12.61%) corresponds to the loss of one guest water and two coordina-



FIG. 3. The solid state luminescent spectrum of **1** upon photoexcitation at 224 nm (color figure available online).

tion water molecules per formula unit ${[Tb(ssa)(H_2O)_2] \cdot H_2O}_n$ upon heating to 235°C, and then hardly any the weight was lost in the range of 235–535°C. The second distinct weight loss of 22.87% (calculated: 25.62%) from 535°C to 684°C corresponds to the loss of half sulfosalicylate ligand per formula unit, which indicates that the framework of $[Tb(ssa)]_n$ collapsed. The final decomposed product presumably is terbium oxide (Tb₄O₇), 56.80% (calculated: 56.30%, based on the remaining mass) (Figure S8).

Fluorescent Properties

Complex 1 displays intricate photoluminescence spectra in the solid state at room temperature. The strong red fluorescent emissions are obtained with many emission peaks, 829 nm (m), 919 nm (s), 949 nm (s), 994 nm (vs), 1054 nm (m), 1084 nm (m), 1111 nm (m), 1117 nm (m), 1267 nm (m), and 1477 nm (m) upon photoexcitation at 224 nm (Figure 3), and the strong



FIG. 4. The solid state luminescent spectrum of **1** upon photoexcitation at 766 nm (color figure available online).

8x10⁴ $^{5}D_{4} \rightarrow ^{7}F_{5}$ 542 7x10 6x10⁴ Emission Intensity 5x10 $4x10^4$ 3x10 wavelength / nn $^{5}D_{1} \rightarrow ^{7}F_{2}$ 2x10 $^{5}D_{4} \rightarrow ^{7}F_{4}$ 488 620 582 1x10 ${}^{5}D_{4} - {}^{7}F_{3}$ 0 -1x10 400 450 500 550 600 650 700 750 800 wavelength / nm

FIG. 5. The solid state luminescent spectrum of **2** (color figure available online).

emission at 67nm upon photoexcitation at 766 nm (Figure 4), respectively. Because free the sulfosalicylic acid ligand exhibits weak emission at 447 nm, the fluorescent emissions of complex **1** may therefore be assigned to the excitation-irradiative energy transfer from different energy level of Nd(III) ions. Comparing with Sm(III), Eu(III), and Tb(III) ions, the little energy gap (ΔE) between the excited state and ground state of 4f-4f orbits for Nd(III) ion results in the complicated fluorescent emissions of **1**, suggesting that **1** may be suitable as a candidate for potential solvent-resistant red fluorescent materials due to its stability and broad photoluminescence in air.^[8,19]

As shown in Figure 5, complex **2** presents four fluorescent emission peaks: 488 nm $({}^{5}D_{4} \rightarrow {}^{7}F_{6}, \text{ mediate})$, 542 nm $({}^{5}D_{4} \rightarrow {}^{7}F_{5}, \text{ strong})$, 582 nm $({}^{5}D_{4} \rightarrow {}^{7}F_{4}, \text{ weak})$, and 620 nm $({}^{5}D_{4} \rightarrow {}^{7}F_{3}, \text{ weak})$, respectively, in the solid state upon photoexcitation at 350 nm. The strong luminescence emission at 542 nm may result from supersensitive effect of the terbium ion.



FIG. 6. Plots of χ_m and $1/\chi_m$ vs T for 1: (\blacksquare) χ_m , (o) $1/\chi_m$, and (-) the best fit obtained (color figure available online).



FIG. 7. Plots of χ_m and $1/\chi_m$ vs T for **2**: (\blacksquare) χ_m and (o) $1/\chi_m$.

The peak positions of fluorescent emission of the Tb compound are consistent with the known ones for free terbium ions, indicating that the effect of the photoluminescence of organic ligands could be negligible in compound **2**.^[20]

Magnetic Properties

The χ_m and $1/\chi_m$ versus T plots for **1** are shown in Figure 6. The room temperature effective moment (μ_{eff}) of 3.55 μ_B is slightly lower than the expected one (3.62 μ_B) for the uncoupled Nd(III) ions, the experimental data well fit Curie-Weiss law with $\theta = -20.33$ K in the measured temperature range, indicating the presence of antiferromagnetic interaction between metal centers. According to the structural data, the bridging carboxylate and hydroxyl groups may be served as the effective pathway of electron transfer for interpreting the magnetic behavior of **1**.^[21]

As shown in Figure 7, the $1/\chi_m$ of complex **2** is rapidly raise with temperature ascent in the low and high temperature ranges, respectively, in which the experimental data well fit Curie-Weiss law with $\theta = -97.28$ K in the range of 5–20 K and $\theta = -329.05$ K in the range of 151–300 K, indicating the presence of antiferromagnetic interaction between metal centers. The room temperature effective moment (μ_{eff}) of 3.24 μ_B is slightly lower than the expected one (3.51 μ_B) for the uncoupled Tb(III) ions, which may result from the effect of 4f-electron spin-orbit coupling interaction.^[22,23]

CONCLUSIONS

Two hybrid polymeric lanthanide complexes have been successfully isolated through hydrothermal reaction. TGA analysis shows high thermal stability of the framework for the title complexes; the luminescent measurement suggests an intense red emission at solid state for **1**. This work may provide useful information for employing multicarboxylate ligands to assemble new lanthanide photoluminescent materials with high thermal stability.

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