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A Self-Assembled Hetero-Bimetallic [Ni(II)-Sm(III)] Coordination Polymer Constructed from a Salamo-Like Ligand and 4,4'-Bipyridine: Synthesis, Structural Characterization, and Properties

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Abstract: An unusual self-assembled hetero-bimetallic [Ni(II)-Sm(III)] coordination polymer, [Ni(L)Sm(NO₃)₃(4,4'-bipy)]_n, is prepared through a hexadentate chelating ligand 2,2'-[1,2-ethylenedioxybis(nitrilomethylidyne)]diphenol (H₂L). The Ni(II)-Sm(III) coordination polymer is validated through elemental analyses, Fourier-transform infrared and UV-Visible spectroscopies, and X-ray single-crystal diffraction. The Ni(II) atom forms a twisted six-coordinated octahedron, and the Sm(III) atom is ten-coordinated, adopting a twisted bicapped square antiprism. An infinite three-dimensional-layer supramolecular structure is obtained through extensive $\pi \cdots \pi$ stacking and intermolecular hydrogen bonding interactions. The polymer has a good antibacterial effect against Staphylococcus aureus.

Keywords: salamo-based compound; coordination polymer; crystal structure; fluorescence; antimicrobial activity

1. Introduction

Salen-based compounds have been reported and studied previously [1–6]. Products gained by the reaction of salicylaldehyde with diamines are significant and common ligands for inorganic and coordination chemistry. The salen-based compounds and their transition metal complexes have attracted increased attention in the last few years. They often have unique crystal structures [7–15], interesting industrial catalyses, and ion recognitions [16–19], including their biological activities [20–27]. Based on the salen-based ligand, new salamo-based ligands were synthesized by introducing -C=N-Ogroups [28–42]. Compared to salen-like compounds, the preparation of Salamo-like compounds is more laborious. Moreover, with the *O*-alkyloxime moiety [$-CH=N-O-(CH_2)_n-O-N=CH-$] replacing the [$-CH=N-(CH_2)_n-N=CH-$] part, the high electronegativity of the oxygen atom can strongly influence the electronic properties of the N₂O₂-donor environment, which can give rise to the novel structures and potential application values of the obtained complexes [1,13]. Their metal complexes studied include supramolecular modes of action, the growth of crystals, and optical and magnetic properties [43–49].

Symmetrical 3-alkoxy salamo-based ligands give relatively easy access to 3d-4f complexes, because the N₂O₂ cavity in the ligand can coordinate with transition metal ions, while the outer coordination



site of the O_4 cavity can accommodate rare-earth elements. Interestingly, anionic and solvent molecules are also coordinated with metal atoms. Transition metal atoms usually form distorted octahedral or triangular biconical configurations, while rare-earth atoms usually form a twisted tricapped trigonal prism with nine-coordination or form a twisted bicapped square antiprismatic coordination arrangement with ten-coordination [47].

According to the previous work of our research group [47], heterobimetallic [Ni(L)Ln] units can be adjusted to form a coordination polymer with a three-dimensional structure by adjusting the ratio of reactants and adding the auxiliary ligand 4,4'-bipyridine. In this paper, the symmetrical 3-MeO hexadentate chelating ligand H₂L was prepared and used for the formation of 3d–4f coordination polymers, together with the exo-dentate auxiliary ligand 4,4'-bipy.

2. Experimental

2.1. Materials and Physical Measurements

3-Methoxysalicylaldehyde (99%) bought from Alfa Aesar (Tianjin, China) was used. The other reagents (Ni(OAc)₂·4H₂O, Sm(NO₃)₃·6H₂O, 4,4'-bipy, and 1,2-dibromoethane) and solvents (ethanol, trichloromethane, etc.) were purchased from Shanghai Darui Chemical Fine Chemicals Company (Tianjin, China), and were of analytical purity.

Elemental analyses for Ni and Sm were carried out on an IRIS ER/SWP-1 ICP atomic emission spectrometer (Elementar, Berlin, Germany). C, H, and N analyses were determined on Elementar GmbH, VarioEL V3.00 automatic elemental analysis equipment (Elementar, Berlin, Germany). Melting points were tested through an X₄ microscopic melting point apparatus (Beijing Taike Instrument Limited Company, Beijing, China).

FT-IR spectroscopy was carried out with a VERTEX70 FT-IR spectrophotometer (Bruker, Billerica, MA, USA, KBr, 400–4000 cm⁻¹).

UV/Vis absorption spectra were recorded by a UV-3900 spectrophotometer (Hitachi, Tokyo, Japan). Fluorescence was measured on an F-7000 FL 220-240V spectrophotometer (Hitachi, Tokyo, Japan). ¹H NMR spectra were measured by a Bruker AVANCE DRX-400 spectrometer (Bruker AVANCE, Billerica, MA, USA).

X-ray single-crystal structure determination was carried out on a Bruker APEX-II CCD diffractometer (Bruker AVANCE, Billerica, MA, USA).

The antimicrobial activities of H₂L, Ni(II) acetate, and the title polymer were tested by a disk diffusion method, *Staphylococcus aureus* being selected as Gram-positive bacteria.

2.2. Preparation of H_2L

The preparation of H_2L is depicted in Scheme 1.



Scheme 1. Synthetic route to H₂L.

First, 1,2-di(aminooxy)ethane was prepared based on a similar method previously reported [47]. 3-Methoxysalicylaldehyde (304.2 mg, 0.02 mmol) was added to 1,2-di(aminooxy)ethane (92.1 mg, 0.01 mmol). The solvent of the two reactants was ethanol, each with a volume of 25 mL. At the temperature of 55– 60 °C, the product was gained by reaction for 7 h. Colorless crystals of the ligand H₂L were obtained by recrystallization from ethanol, yield: 85%.m.p: 130–132 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 3.90 (s, 6H, –OMe), 4.48 (s, 4H, –CH₂), 6.82 (dd, *J* = 7.9, 1.9 Hz, 2H, –ArH), 6.87 (t, *J* = 7.9 Hz, 2H, –ArH), 6.90 (dd, *J* = 7.9, 1.9 Hz, 2H, –ArH), 8.25 (s, 2H, –N=CH), 9.75 (s, 2H,–OH). Anal. Calcd. for C₁₈H₂₀N₂O₆ (%): C 59.99; H 5.59; N 7.77. Found C 60.22; H 5.67; N 7.53.

2.3. Preparation of the Ni(II)-Sm(III) Polymer

An ethanol solution (2 mL) of Ni(OAc)₂·4H₂O (2.49 mg, 0.01 mmol) and an ethanol solution (2 mL) of Sm(NO₃)₃·6H₂O (4.45 mg, 0.01 mmol) were successively added to a trichloromethane solution (2 mL) of H₂L (3.60 mg, 0.01 mmol), and the same amount of ethanol solution (2 mL) of 4,4'-bipy (1.56 mg, 0.01 mmol) was then added to the mixture. After stirring for ten minutes, the mixed solution was filtered. After standing for ten days, several colorless block-shaped single crystals were obtained by natural evaporation (Scheme 2). Yield: 37%. Anal. Calcd. for C₂₈H₂₆SmN₇NiO₁₅ (%): C 36.97; H 2.88; N 10.78; Ni 6.45; Sm 16.53. Found C 34.88; H 2.79; N 10.81; Ni 6.43; Sm 16.46.



Scheme 2. Synthetic route to the title polymer.

2.4. Crystal Structure Determination of the Ni(II)-Sm(III) Polymer

The crystal structure was obtained by X-ray single-crystal diffraction on a Bruker APEX-II CCD diffractometer (Table 1). The X-ray single-crystal diffraction data of the Ni(II)-Sm(III) polymer were recorded and collected by using a Bruker APEX-II CCD diffractometer with Mo-K α radiation (λ = 0.71073 Å), and corrected via the Lorentz and polarization factor with a multi-scan method. The program SHELXS-2018 and Fourier difference techniques were used to solve the structure. It was corrected via the full-matrix least-squares on F^2 . The structure included a large void, and the positive or negative ions and the solvent water molecules in the void could not be confirmed, owing to it being highly disordered. Thus, SQUEEZE in the PLATON program was used to remove the highly disordered ions and solvent. (Solvent Accessible Volume = 1275, Electrons Found in S.A.V. = 133). Anisotropic displacement parameters were applied for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model.

Polymer	The [Ni(II)-Sm(III)] Coordination Polymer		
Empirical formula	C ₂₈ H ₂₆ N ₇ NiO ₁₅ Sm		
Formula weight	909.62		
Т, К	173(2)		
Radiation; wavelength (Å)	Μο Κα; 0.71073		
Crystal system	monoclinic		
Space group	P2 ₁ /c		
a, Å	11.3928(4)		
b, Å	19.4539(7)		
c, Å	19.4229(8)		
β, deg	98.689(2)		
Volume, Å ³	4255.4(3)		
Z	4		
D_{calcd} , g cm ⁻³	1.42		
Crystal size, mm ³	$0.18\times0.20\times0.22$		
Absorption coefficient, mm ⁻¹	1.9		
range data collection, deg	2.400 to 26.000		
F(000), e	1812		
hklrange	±14, ±24, ±24		
Refl. collected/unique/R _{int}	60159/9380/0.0196		
Data/restraints/ref. parameters	9380/11/471		
Final R1/wR2 [I > 2 σ (I)] ^{a,b}	0.0332/0.1039		
Final R1 wR2(all data) ^{a,b}	0.0405/0.1063		
GoF ^c	0.989		
$\Delta \rho_{max/min}$, e Å ⁻³	1.02/-1.01		

Table 1. Crystal data and structure refinement for the title polymer.

^a R1 = $\Sigma ||F_0| - |F_c||/\Sigma |F_0|$; ^b wR2 = [\ddot{y} w($F_0^2 - F_c^2$)²/ \ddot{y} w(F_0^2)²]^{1/2}, w = [$\sigma^2(F_0^2) + (AP)^2 + BP$]⁻¹, where P = (Max($F_0^2, 0) + 2F_c^2$)/3; ^c GoF = S = [\ddot{y} w($F_0^2 - F_c^2$)²/($n_{obs} - n_{param}$)]^{1/2}.

CCDC 1939692 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac. uk/data_request/cif.

3. Results and Discussion

 H_2L and the title polymer have been gained and validated by IR spectra, UV/Vis absorption spectra, and X-ray single-crystal diffraction and fluorescence spectra. Their antimicrobial activities were investigated. The compounds were stable in air.

3.1. PXRD Analysis

A PXRD test was conducted for the title polymer to demonstrate whether the structure is truly representative. The PXRD result of the title polymer is given in Figure 1. Through detailed comparison, the experimental result is coincident with the simulation result. Therefore, the synthesized samples have high purity and can be used for further study of spectral characterization and fluorescence properties.



Figure 1. Comparing the simulated PXRD and experimental patterns of the [Ni(II)-Sm(III)] coordination polymer.

3.2. FT-IR Spectra of H₂L and the Title Polymer

The FT-IR spectra of H_2L and the title polymer are depicted in Figure 2.



Figure 2. Infrared spectra of H₂L and its Ni(II)-Sm(III) coordination polymer.

The band of H₂L appearing at 3437 cm⁻¹ is attributed to the O-H stretching band [47]. The characteristic C=N stretching band is found at approximately 1606 cm⁻¹ in the spectrum of H₂L, and moves to a lower frequency in the polymer, indicating the metal coordination at the nitrogen atoms of oxime groups [15,50]. The Ar–O stretching vibration band of H₂L emerges as an intensive band at 1253 cm⁻¹ as reported for analogous salen-based compounds [6,28,43], while the title polymer shows this band at 1210 cm⁻¹, again due to complexation.

3.3. Description of the Molecular Structure of the Title Polymer

The structure of the heterobimetallic [Ni(II)-Sm(III)] salamo-based coordination polymer is depicted in Figure 3, complemented by data in Table 2.



Figure 3. (**a**) Molecular structure and atom numberings of the title polymer. (**b**) Coordination polyhedra for Sm(III) and Ni(II) atoms in the title polymer.

The title polymer crystallizes in the monoclinic space group $P2_1/c$ with Z = 4, consisting of one Sm(III) atom, one Ni(II) atom, one deprotonated (L)^{2–} unit, one 4,4'-bipyridine ligand, three bidentate chelating nitrate anions, and three water molecules.

Each Ni(II) (Ni1) atom is sited in a N₂O₂-donor cavity of the salamo ligand, and is octahedrally hexacoordinated by two oxime N atoms (N2 and N1), two phenoxo O atoms (O5 and O2), and two N atoms (N4 or N3) from two 4,4'-bipyridine ligands [50]. The equatorial coordination sites have distances Ni1–N2 = 2.030(4) Å, Ni1–N1 = 2.072(4) Å, Ni1–O2 = 2.0370(19) Å, and Ni1–O5 = 2.0399(19) Å, and the axial positions are at the distances Ni1–N4 = 2.167(2) and Ni1–N3 = 2.172(2) Å (Table 2).

The Sm(III) is surrounded by an O_{10} environment containing four O atoms (O6, O5, O2, and O1) from the (L)^{2–} units and six O atoms (O14, O13, O11, O10, O8, and O7) from the three bidentate nitrate ligands. The decacoordinated Sm(III) atom possesses a geometry of a twisted bicapped square antiprism. The Sm–O distance is in the normal range of 2.353(2)–2.653(4) Å.

Bond	Lengths	Bond	Lengths	Bond	Lengths
Sm1-O1	2.653(4)	Sm1-O10	2.617(4)	Ni1-N1	2.072(4)
Sm1-O2	2.353(2)	Sm1-O11	2.518(4)	Ni1-N2	2.030(4)
Sm1-O5	2.416(2)	Sm1-O13	2.510(3)	Ni1-N3	2.172(2)
Sm1-O6	2.6013(19)	Sm1-O14	2.481(2)	Ni1-N4 #1	2.167(2)
Sm1-07	2.529(3)	Ni1-O2	2.0370(19)		
Sm1-O8	2.463(4)	Ni1-05	2.0399(19)		
Bond	Angles	Bond	Angles	Bond	Angles
O1-Sm1-O2	61.11(7)	O5-Sm1-O10	173.74(9)	O10-Sm1-O13	63.93(10)
O1-Sm1-O5	117.08(7)	O5-Sm1-O11	124.32(10)	O10-Sm1-O14	102.11(9)
O1-Sm1-O6	143.61(9)	O5-Sm1-O13	114.44(8)	O11-Sm1-O13	73.92(12)
O1-Sm1-O7	71.32(11)	O5-Sm1-O14	73.25(7)	O11-Sm1-O14	73.63(10)
O1-Sm1-O8	78.12(11)	O6-Sm1-O7	73.41(10)	O13-Sm1-O14	51.02(7)
O1-Sm1-O10	64.15(10)	O6-Sm1-O8	73.12(10)	O2-Ni1-O5	78.33(8)
O1-Sm1-O11	72.52(11)	O6-Sm1-O10	121.02(9)	O2-Ni1-N1	90.31(12)
O1-Sm1-O13	128.07(9)	O6-Sm1-O11	140.94(10)	O2-Ni1-N2	167.66(12)
O1-Sm1-O14	143.78(9)	O6-Sm1-O13	69.80(10)	O2-Ni1-N3	90.61(12)
O2-Sm1-O5	65.35(7)	O6-Sm1-O14	72.59(7)	O2-Ni1-N4 ^{#1}	89.60(12)
O2-Sm1-O6	126.96(7)	O7-Sm1-O8	51.43(10)	O5-Ni1-N1	168.08(12)
O2-Sm1-O7	88.84(9)	O7-Sm1-O10	108.73(9)	O5-Ni1-N2	90.42(12)
O2-Sm1-O8	131.26(10)	O7-Sm1-O11	143.58(12)	O5-Ni1-N3	87.88(12)
O2-Sm1-O10	111.99(10)	O7-Sm1-O13	127.65(10)	O5-Ni1-N4 #1	95.18(12)
O2-Sm1-O11	77.41(10)	O7-Sm1-O14	142.47(9)	N1-Ni1-N2	101.20(15)
O2-Sm1-O13	143.33(9)	O8-Sm1-O10	66.71(12)	N1-Ni1-N3	88.64(14)
O2-Sm1-O14	99.12(7)	O8-Sm1-O11	116.21(12)	N1-Ni1-N4 ^{#1}	88.27(14)
O5-Sm1-O6	62.10(6)	O8-Sm1-O13	82.62(10)	O10-Sm1-O13	94.07(14)
O5-Sm1-O7	77.17(7)	O8-Sm1-O14	129.42(10)	O10-Sm1-O14	86.35(14)
O5-Sm1-O8	119.44(10)	O10-Sm1-O11	49.60(12)	O11-Sm1-O13	176.91(14)

Table 2. Selected bond lengths (Å) and angles (deg) for the title polymer.

Symmetry transformations used to generate equivalent atoms: $^{#1}$ 1 + x, y, z.

3.4. Supramolecular Interactions in the Title Polymer

As is depicted in Figure 4, complemented by data in Table 3, in the title polymer structure, five of the couples are weak intramolecular hydrogen bonds (C1–H1B···O10, C9–H9A···N3, C23–H23···O2, C28–H28···O7, and C24–H24···N1) and two intermolecular hydrogen bonds (C4–H4···O9 and C9–H9B···O13), which indicate that the supramolecular interactions exist in the title polymer [51–56]. The donor (C1–H1B) from the 3-methoxy substituent group from the (L)^{2–} moiety forms a hydrogen bond with an O atom (O10) of one bidentate chelating nitrate as a hydrogen bonding receptor. The donors (C23–H23, C24–H24, and C28–H28) of the 4,4'-bipy moieties form intermolecular hydrogen bond interactions with O and N atoms (O2, N1 and O7) of the fully deprotonated (L)^{2–} moieties as hydrogen bond receptors. The donor (C9–H9A) of the (L)^{2–} unit is contained in the hydrogen bond interaction with the N atom (N3) of the 4,4'-bipy ligand as a hydrogen bonding receptor. These ligands are connected by C–H··· π (C19–H19···Cg2) interactions (Figure 5), forming a one-dimensional chain structure (Figure 6).



Figure 4. View of the intramolecular hydrogen bond interactions of the Ni(II)-Sm(III) polymer (hydrogen atoms are omitted for clarity, except those forming hydrogen bonding).

Table 3. Hydrogen bonding interactions (Å, °) and C-H… π stacking interactions for the Ni(II)-Sm(III) polymer.

D−H…A.	d(D-H)	d(H…A)	d(D…A)	∠D–H…A	Symmetry Code		
C1-H1B…O10	0.98	2.39	2.897(7)	111			
C4-H4…O9	0.95	2.55	3.365(5)	143	x, 3/2 - y, 1/2 + z		
C9-H9A…N3	0.99	2.44	3.357(5)	154			
C9-H9B…O13	0.99	2.40	3.230(5)	141	1 - x, -1/2 + y, 3/2 - z		
C23-H23-O2	0.95	2.58	3.093(4)	114			
C24-H24…N1	0.95	2.61	3.104(5)	113	-1 + x, y, z		
C28-H28-O7	0.95	2.25	3.120(5)	151	-1 + x, y, z		
C19-H19…Cg2	0.98	2.56	2.897(7)	114	<i>x, y, z</i>		
Cg6…Cg6			4.065(2)				
Cg6 = C12-C13-C14-C15-C16-C.							



Figure 5. View of the intramolecular C–H… π interactions.



Figure 6. View of one-dimensional chain-like structure of the title polymer.

The π ··· π stacking interactions depicted in Figure 7 (Cg6···Cg6) (Cg6 = C17–C16–C15–C14–C13–C12), and the intermolecular hydrogen bond interactions (C4–H4···O9 and C9–H9B···O13) depicted in Figure 8 give rise to the formation of a 2D supramolecular network, further linking into a 3D supramolecular structure by C–H··· π , π ·· π , and hydrogen-bond interactions [57–64] (Figure 9).



Figure 7. View of the π ··· π stacking interactions.



Figure 8. View of two-dimensional supramolecular network of the title polymer, combined by intermolecular hydrogen bondings.



Figure 9. View of the three-dimensional supramolecular structure of the title polymer.

3.5. Molar Conductance and Solubility and Mass Spectrometry Analysis of the Title Polymer

The [Ni(II)-Sm(III)] coordination polymer could be soluble in DMSO and DMF, slightly soluble in ethanol, methanol, THF, dichloromethane, trichloromethane, acetonitrile, and acetone, and insoluble in n-hexane, ethyl ether, and water. Molar conductance of the title polymer in DMF at 25 °C $(1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1})$ is 179.6 $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$. The result of molar conductivity is inconsistent with the 1:2 electrolyte reported previously [50].

According to the data analysis of mass spectrometry (Figure S1), when m/z = 418.9292, which is almost equal to the relative molecular mass of [NiL], when m/z = 158.9381, it is the relative molecular mass of 4,4'-bipy, indicating that 4,4'-bipy exists in the solution in the free form, while samarium nitrate might exist in the solution in the form of $[Sm(NO_3)(DMF)_3]^{2+}$ due to the peak of m/z = 430.9834.

Through conductivity tests and mass spectrometry, we determined that the [Ni(II)-Sm(III)] coordination polymer dissolved in DMF may comprise [Ni(L)], 4,4'-bipy, [Sm(NO₃)(DMF)₃]²⁺ cation, and NO₃⁻ anions. The observed conductance would then result from the presence of $[Sm(NO_3)(DMF)_3]^{2+}$ cation and NO₃⁻ anions, according to the following equilibria taking place in solution:

 $[Ni(L)Sm(NO_3)_3(4,4'-bipy)]_n \rightleftharpoons n[Ni(L)Sm(NO_3)_3(4,4'-bipy)]$

 $[Ni(L)Sm(NO_3)_3(4,4'-bipy)] + DMF \rightleftharpoons [Ni(L)] + 4,4'-bipy + [Sm(NO_3)_3(DMF)]$

 $[Sm(NO_3)_3(DMF)] + 2DMF \rightleftharpoons [Sm(NO_3)(DMF)_3]^{2+} + 2NO_3^{-1}$

3.6. UV/Vis Absorption Spectra of H₂L and the Title Polymer

The UV/Vis absorption spectra of H_2L and the title polymer (in 10^{-5} M ethanol solution) are depicted in the Figure 10.



Figure 10. The UV/Vis absorption spectra of H_2L , its Ni(II)-Sm(III) coordination polymer, Ni(OAc)₂·4H₂O, Sm(NO₃)₃·6H₂O, and 4,4'-bipy.

The characteristic peaks of H₂L appear at approximately 317, 271, and 223 nm, respectively, the peaks at 271 and 223 nm could be ascribed to the π - π * transition of the benzene ring, and the peak at 317 nm could be attributed to the intraligand π - π * transition of the oxime-like group [20,47]. Compared to the peaks of H₂L, the absorptions of the polymer bathochromically move to approximately 228 and 276 nm, exhibiting coordination of the (L)²⁻ unit to the Ni(II) atom [15,50]. Upon coordination, the intra-ligand π - π * transition of the oxime-like group disappeared again, indicating the complexation [47,50]. A new characteristic peak at approximately 350 nm is found for the coordination polymer, belonging to an n- π * charge transfer of the imino group [43,50].

In order to further prove that the polymer in the form of a solution is not affected by metal ions, 4,4'-bipy, we conducted UV spectrum experiments on its solution (Ni(OAc)₂·4H₂O, Sm(NO₃)₃·6H₂O, and 4,4'-bipy in 10^{-5} M EtOH). There was almost no change in the absorbance value of metal ions and no characteristic absorption peak. Further, 4,4'-bipy showed a characteristic absorption peak at 239 nm.

3.7. Fluorescence Properties of the Title Polymer

The fluorescence spectra of H₂L and the [Ni(II)–Sm(III)] polymer in EtOH (1.0×10^{-5} M) are shown in Figure 11. The results show that H₂L presents an intensive photoluminescence with maximum emission at approximately 395 nm at 311 nm excitation, which can be explained as the π – π * transition in H₂L. In the title polymer, the emission peak appears at approximately 382 nm, and there is a slight blue shift compared to H₂L [50], the fluorescence intensity of the title polymer appears to be quenched, and at the same time, it can be seen from the data of the mass spectrum that the polymer solution is almost in the form of [Ni(L)] + 4,4'-bipy + [Sm(NO₃)(DMF)₃], indicating that the coordinated Ni(II) ion has a heavy atom effect [62]. The high nuclear charge of the Ni(II) causes the electronic energy levels of the phosphorescent molecules to be staggered, which enhances the spin–orbit coupling of the phosphorescent molecules, thereby increasing the probability of inter-system hopping (ISC) of S1→TI, thereby quenching the fluorescence. In the fluorescence spectra, only the band at approximately 375–650 nm instead of the f–f emission is expected for Sm(III) ions.





Figure 11. Photophysical properties of H₂L and its corresponding Ni(II)-Sm(III) polymer in ethanol (1 $\times 10^{-5}$ mol L⁻¹) at 311 nm excitation.

3.8. Antimicrobial Activity

Firstly, the Staphylococcus aureus on the plate was inoculated into Agar (2%) (LB) medium for overnight culture, and 0.1 mL of night-cultured fresh bacterial suspension was added to the LB medium after autoclaving and cooling to 50 °C. Secondly, after the mixture was mixed well, LB solid AGAR was poured into a sterile Petri dish. After being completely solidified, we punched holes in the LB medium with a perforator. Finally, DMF sample solutions were configurated with solution gradients of four various concentrations (0.35, 0.7, 1.4, and 2.8 mg mL⁻¹).

Then, 70 μ L of samples with different concentrations were added to the samples with a pipette gun. After an eight-hour incubation period at 37 °C, diameters of the inhibition zones were measured. The experimental results are compared to Ampicillin as a reference standard with various concentrations. The diameters of the inhibition zones of H₂L, nickel acetate, and the title polymer are shown in Figure 12. The title polymer shows a more enhanced antibacterial effect than H₂L and the metal salt solution under the same conditions. At the same time, the complex [NiL] also has a certain antibacterial activity, but it is not as high as that of the coordination polymer, which may be due to the antibacterial activity of the dissolved polymer being the sum of the comprehensive activities of various components. It can be conjectured from the experimental results and previous literature [54], first of all, that this is the result of the destruction of the protein structure in bacteria due to the action of heavy metal ions in coordination polymers [32]. Secondly, the ligand H₂L destroys part of the cell membrane, making the bacteria unable to further divide and reproduce, leading to death. These results are similar to biological activities of related Schiff base complexes previously reported [65].



Figure 12. Inhibition of the Staphylococcus aureus at different concentrations.

4. Conclusions

A new heterobimetallic Ni(II)-Sm(III) polymer has been prepared and structurally validated, in which H₂L represents a symmetric salamo-based bisoxime ligand. In the Ni(II)-Sm(III) polymer, the hexacoordinated nickel(II) atom bears a slightly twisted octahedral geometry, and the decacoordinated Sm(III) atom possesses a twisted bicapped square antiprismatic arrangement. In the crystal, the polymer forms a self-assembling infinite 2D network further linking into a 3D supramolecular structure by C–H··· π , π ··· π , and hydrogen-bond interactions. Compared to H₂L, the Ni(II)-Sm(III) polymer exhibits only a very slightly hypsochromically shifted fluorescence of lower intensity, indicating that the coordinated Ni(II) cation has a minor heavy atom effect. Antimicrobial experiments have shown that the title polymer demonstrates stronger antimicrobial activity than H₂L under the same conditions.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4352/10/7/579/s1, Figure S1: Mass spectrogram of Ni(II)-Sm(III) coordination polymer solution.

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