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Syntheses, structures, and supra-molecular assembles of zinc 4-sulfobenzoate complexes with chelating and/or bridging ligands

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ABSTRACT

Three unique $Zn^{II}/4$ -sulfobenzoate complexes based on 2,2'-bipyridine and/or 4,4'-bipyridine, [Zn(4-sb)(2,2'-bipy)(H₂O)₃]·H₂O (**1**), {[Zn(4,4'-bipy)(H₂O)₄]·(4-sb)]_n (**2**), and {[Zn(4-sb)(2,2'-bipy)(4,4'-bipy)_{0,5}(-H₂O)]·2H₂O]_n (**3**) [4-sb = 4-sulfobenzoate; 4,4'-bipy = 4,4'-bipyridine; 2,2'-bipy = 2,2'-bipyridine], have been prepared and characterized by single-crystal X-ray analyses, elemental analyses, IR, thermogravimetric analyses and fluorescent spectra. The molecular structure of the complex **1** is a monomer species, while the structures of complexes **2** and **3** are 1-D chains. The complex **2** is a cation–anion species. These extended hydrogen-bonding networks are 3-D architectures. In complexes **1** and **3** there are strong π ... π stacking effects, while in complex **2** there is no such interaction. The thermal stability of complexes **1**, **2**, and **3** has the order of **2** > **1** > **3**.

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1. Introduction

In recent years, diverse metal complexes have attracted considerable attention due to their potential functional applications strongly related to their structures [1-4]. Many factors can influence the synthesis of diverse metal complexes, such as metal ions, coordination features of the ligands, starting materials, pH, temperature, synthetic methods, and templates [5–10]. Diverse structures, in general, show different supra-molecular building blocks, different hydrogen-bonding patterns, and different weak interactions, therefore careful tune of the diverse structures will construct specific functional materials [11,12]. The 4-sulfobenzoate ligand with two different functional groups have been used to produce several interesting metal complexes in our lab and our results showed that this ligand performs abundant bonding modes, coordination sites and bonding directions [13-19]; therefore the 4-sulfobenzoate is a good candidate for constructing diverse metal complexes. On the other hands, the coordination modes of 4-sulfobenzoate ligand with metal ions can be adjusted by the addition of the neutral ligands; such effect further results in abundant diverse structures. For the reasons above mentioned, we choose 4-sulfobenzoate ligand with fixed metal ion, zinc, but used the combination of 2,2'-bipyridine and/or 4,4'-bipyridine to synthesize novel diverse complexes. Herein, we report syntheses, structures, properties, and supra-molecular assembles of three new complexes, namely, $[Zn(4-sb)(2,2'-bipy)(H_2O)_3] \cdot H_2O(1)$, $\{[Zn(4,4'-bipy)(H_2O)_4](4-sb)\}_n$ (**2**), and $[Zn(4-sb)(2,2'-bipy)(4,4'-bipy)_{0.5}(H_2O)]_n \cdot 2H_2O$ (**3**).

2. Experimental

2.1. Materials and physical measurements

Chemicals and solvents used in the experiments were obtained from commercial sources and were used as received without purification. C, H, and N elemental analyses were carried out on a Perkin–Elmer analyzer model 1110. The IR spectra were taken on a Nicolet Nexus 470 IR spectrophotometer as KBr pellets in the 400–4000 cm⁻¹ region. Thermogravimetric analyses (TGA) were studied by a Delta Series TA-SDT Q600 in a N₂ atmosphere in the temperature range between room temperature and 800 °C at a heating rate of 10 °C min⁻¹ using Al₂O₃ crucibles. The fluorescent study was carried out on a powdered sample in the solid state at room temperature using a Hitachi 850 spectrometer.

2.2. Synthesis of $[Zn(4-sb)(2,2'-bipy)(H_2O)_3] \cdot H_2O(1)$

A mixture of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.112 g, 0.5 mmol), 4-sulfobenzoic acid mono-potassium salt (0.120 g, 0.5 mmol), 2,2'-bipyridine (0.078 g, 0.5 mmol) and 15 ml H₂O was placed in a 30 ml Teflon-lined stainless-steel and heated at 433 K for 3 days. The vessel was slowly cooled to room temperature, and then filtered and the filtrate was standing for 15 days and colorless brick crystals of **1** were obtained. Yield: 24% based on zinc salt. Anal. Calcd. for



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 $\begin{array}{l} C_{17}H_{20} N_2 O_9 ZnS: C, 41.35\%; H, 4.08\%; N, 5.67\%; found: C, 41.42\%; H, \\ 4.10\%; N, 5.58\%. IR (KBr pellet, cm^{-1}): 3377(s), 1599(s), 1552(m), \\ 1493(w), 1476(w), 1444(s), 1401(s), 1317(w), 1220(s), 1186(s), \\ 1010(s), 868(w), 767(s), 736(s), 702(m), 643(m), 565(m). \end{array}$

2.3. Synthesis of $\{[Zn(4,4'-bipy)(H_2O)_4] \cdot (4-sb)\}_n$ (2)

A mixture of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.112 g, 0.5 mmol), 4-sulfobenzoic acid mono-potassium salt (0.120 g, 0.5 mmol), 4,4'-bipyridine (0.078 g, 0.5 mmol) and 15 ml H₂O was placed in a 30 ml Teflon-lined stainless-steel and heated at 433 K for 3 days. The vessel was slowly cooled to room temperature, and then filtered and the filtrate was standing for 2 days. Colorless crystal of **2** was obtained. Yield: 37% based on zinc salt. Anal. Calcd. for $C_{17}H_{20}$ N₂O₉ZnS: C, 41.35%; H, 4.08%; N, 5.67%; found: C, 41.33%; H, 4.08%; N, 5.62%. IR (KBr pellet, cm⁻¹): 3301(s), 1613(s), 1545(m), 1498(w), 1421(m), 1377(s), 1228(s), 1176(s), 1115(s), 1034(s), 1010(s), 883(w), 820(m), 795(m), 734(s), 706(w), 636(s), 571(w).

2.4. Synthesis of $[Zn(4-sb)(2,2'-bipy)(4,4'-bipy)_{0.5}(H_2O)]_n \cdot 2H_2O$ (3)

A mixture of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.112 g, 0.5 mmol), 4-sulfobenzoic acid mono-potassium salt (0.120 g, 0.5 mmol), 2,2'-bipyridine (0.078 g, 0.5 mmol), 4,4'-bipyridine (0.078 g, 0.5 mmol) and 15 ml H₂O was placed in a 30 ml Teflon-lined stainless-steel and heated at 433 K for 3 days. After cooled to room temperature, colorless block crystal was obtained from the vessel. Yield: 45% based on zinc salt. Anal. Calcd. for $C_{22}H_{22}N_3SZnO_8$: C, 47.71%; H, 4.00%; N, 7.59%; found: C, 47.78%; H, 4.23%; N, 7.33%. IR (KBr pellet, cm⁻¹): 3427(s), 1609(s), 1551(s), 1491(m), 1478(m), 1446(m), 1403(s), 1320(w), 1229(s), 1183(s), 1162(s), 1143(m), 1119(s), 1071(w), 1036(s), 1024(m), 1008(s), 810(m), 779(s), 766(s), 737(s), 698(m), 642(m), 632(m), 568(w).

2.5. Single-crystal structure determination

Crystals with suitable sizes of **1–3** were selected for data collection by a Bruker Smart CCD area detector with graphite monochro-

matized Mo K α radiation (λ = 0.71073 Å). The data were integrated by use of the SAINT program [20] and this program also did the intensities corrected for Lorentz and polarization effects. The absorption corrections were done by the SADABS program [21]. All of these three structures were solved initially by direct methods and then completed by full matrix least squares on F^2 followed by difference Fourier synthesis using the SHELXL-97 program [22] in the WinGX environment [23]. In all three structures, the nonhydrogen atoms were refined with anisotropic displacement parameters. The O5 atom is disordered over two positions with the ratio of 0.51(7): 0.49(7) in complex **1**. Hydrogen atoms bonded to the carbon atoms were placed in calculated positions and refined as riding, with C–H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The water hydrogen atoms were located in the difference Fourier maps and refined with an O–H distance restraint of 0.85(1) Å. The drawings of the three molecules were realized with the help of ORTEP-3 for Windows [24] and Mercury software [25]. Crystallographic data and refinement parameters for these three complexes are given in Table 1.

3. Results and discussion

3.1. Synthesis

In our lab, we have synthesized the complex $[Zn(4,4'-bipy)_2(H_2O)_4]\cdot 2(4-Hsb)$ (**4**), in which the 4-sulfobenzoate is partly deprotonated and exists as a non-coordinating anion [17]. Our target was to obtain the full deprotonation 4-sb, therefore the further exploration was done. The synthesis of complex **4** was achieved by using the starting material $ZnSO_4 \cdot 7H_2O$. The $Zn(CH_3COO)_2 \cdot 2H_2O$ used in the new procedure led to the precipitation of complex **2**. In complex **2**, although the 4-sb is fully deprotonated, it is still a non-coordinating anion. Considering the coordination behavior of 4-sb in 2,2'-bipyridine zinc complex, **1**, we combined the 2,2'-bipy and 4,4'-bipy to synthesize novel complex with the coordination of 4-sb to the metal ion. The hydrothermal synthesis led to novel complex, **3**, in which the complex contains both chelating and bridging ligands.

Table 1

Crystallographic data and refinement parameter for complexes 1, 2, and 3.

Complex	1	2	3
Empirical formula	C ₁₇ H ₂₀ N ₂ O ₉ SZn	C ₁₇ H ₂₀ N ₂ O ₉ SZn	C22H22N3O8SZn
Formula	493.78	493.78	553.86
Crystal color/shape	Colorless/brick	Colorless/block	Colorless/block
Crystal size/mm	$0.31 \times 0.24 {\times} 0.22$	$0.37 \times 0.28 \times 0.23$	$0.33 \times 0.21 \times 0.19$
Space group	Monoclinic, P2 ₁ /n	Triclinic, P1	Triclinic, PĪ
a (Å)	11.7796(10)	7.3840(7)	8.8716(25)
b (Å)	11.2355(9)	10.5394(9)	9.8863(28)
c (Å)	16.3836(13)	13.5034(12)	13.5952(36)
α (°)	90	67.387(1)	86.793(8)
β (°)	104.398(1)	83.674(1)	89.864(8)
γ (°)	90	78.483(1)	79.971(8)
V (Å ³)	2100.3(3)	949.91(15)	1172.3(6)
Ζ	4	2	2
D (g cm ⁻³)	1.562	1.726	1.569
T (K)	295(2)	295(2)	295(2)
μ (mm ⁻¹)	1.320	1.459	1.190
θ range (°)	2.2–27.5	2.1-25.3	1.5-25.0
Measured reflections	12842	5037	9711
Unique reflections	4804	3382	3755
Observed reflections	3908	3096	2806
F (0 0 0)	1016	508	570
R_1 and $wR_2 (I > 2\sigma (I))$	0.030, 0.084	0.024, 0.071	0.048, 0.152
R_1 and wR_2 (all data)	0.041, 0.093	0.027, 0.075	0.073, 0.212
Number of variable	306	295	334
Goodness of fit (GOF)	0.811	0.842	1.262
Largest difference peak and hole (e $Å^{-3}$)	0.345, -0.379	0.344, -0.355	0.642, -0.784



Fig. 1. ORTEP view of the molecular structure of complex 1. Hydrogen atoms are omitted for clarity.

3.2. Description of the molecular structures

The molecular structure of complex **1** is a monomer (Fig. 1 and Table 2), while complexes **2** and **3** are 1-D chains (Figs. 2 and 3; Tables 3 and 4). In these three complexes, zinc ions adopt octahedron geometries. The zinc coordination geometry in **1** is completed by two N atoms of one 2,2'-bipyridne, one O atom from the 4-sb, and three O atoms from three water molecules. The Zn–O bond distances in **1** range from 2.0716(15) Å to 2.1474(15) Å. The Zn–N bond lengths are in agreement with those of Zn(II) complexes containing 2,2'-bipyridine [26,27].

The complex **2** is a cation–anion species (Fig. 2a). The cationic motif (Fig. 2b), $[Zn(4,4'-bipy)(H_2O)_4]^{2^+}$, is a 1-D chain in which the 4,4'-bipyridine is a polymeric bridging ligand and such motif has been reported by others [28]. The separation distance of Zn. ..Zn between 1-D chains is 7.0275(6) Å. The pyridyl rings of the 4,4'-bipyridine ligands are not coplanar with a dihedral angle of 12.7(1)°. The 4-sb in complex **2** is fully deprotonated but uncoordinated and only serves as a counter-ion. The bond lengths of Zn–O range from 2.0977(14) Å to 2.1875(15) Å which are compared well with those distances reported for other Zn^{II}-aqua (2.12–2.19 Å) complexes [28–30]. The bond distances of Zn–N are typical for Zn^{II} compounds with 4,4'-bipyridine [31,32]. The separation of Zn. ..Zn by 4,4'-bipyridine ligand in the cationic chain is 11.3649 (8) Å which is shorter than those of previous reports [28].

The X-ray single-crystal analysis reveals complex **3** is a zig-zag chain linked by 4-sb and 4,4'-bipy (Fig. 3a). Unlike complexes **1** and

Table 2							
Selected	bond	lengths	(Å) and	angles	(°) in	complex	1.

Zn1-02	2.0730(14)	Zn1-06	2.1394(15)
Zn1-07	2.1474(15)	Zn1-08	2.0716(15)
Zn1-N1	2.1273(17)	Zn1-N2	2.1411(18)
02-Zn1-06	90.76(5)	02-Zn1-07	88.80(6)
02-Zn1-08	94.03(7)	02-Zn1-N1	92.21(6)
02-Zn1-N2	169.44(7)	06-Zn1-07	175.07(6)
06-Zn1-08	89.21(6)	06-Zn1-N1	93.71(6)
06-Zn1-N2	89.51(6)	07-Zn1-08	85.93(6)
07-Zn1-N1	91.21(6)	07-Zn1-N2	91.82(6)
08-Zn1-N1	173.08(7)	08-Zn1-N2	96.53(7)
N1-Zn1-N2	77.24(7)		

2, the 4-sb in **3** bis-monodentately acts as a bridge by two O atoms from carboxyl group and sulfonate group and the 4,4'-bipyridine is only a dimeric ligand linking Zn^{II} ions. The bond lengths of $Zn-N_{2,2'-bipy}$ are a little bit longer than that in complex **1** and bond lengths of $Zn-N_{4,4'-bipy}$ are longer than that in complex **2**. The bond lengths of Zn-O are consistent with other two complexes, **1** and **2**. The distances of Zn...Zn separated by 4-sb and 4,4'-bipyridine are 9.539(2) Å and 11.433(2) Å (longer than that in complex **1**), respectively.

The addition of neutral ligands in $Zn^{II}/4$ -sb system leads to different supra-molecular assembles. All 4-sb ligands in these three complexes are fully deprotonated and perform three different coordination modes, monodentate in **1**, free ligand in **2**, and bismonodentate in **3**. The 4,4'-bipy ligands in **2** act as polymeric linkers while in complex **3** the 4,4'-bipy ligand serves as a dimeric bridge. And in complex **4**, $[Zn(4,4'-bipy)_2(H_2O)_4]\cdot 2(4-Hsb)$, the 4,4'-bipy is only a monodentate terminal ligand. Therefore, careful control or tune of synthetic procedures results in abundant diverse metal complexes.

3.3. Hydrogen bonds and $\pi - \pi$ stacking interactions

In complex **1**, there is one intra-molecular hydrogen bond between coordinated water molecule and carboxyl group. There are abundant inter-molecular O–H···O hydrogen bonds between coordinated water molecules and carboxyl groups, sulfonate groups, and lattice water molecules, respectively, and between sulfonate groups and lattice water molecules. These hydrogen-bonding interactions extend the monomer structure into 3-D architecture (Fig. 4). Within the 3-D framework, face to face π – π interactions occur between rings of symmetry-related 2,2'-bipyridine ligands with a centroid-to-centroid distance of 3.7721(15) Å and between 2,2'-bipy (the ring of N1/C1–C5) and 4-sb (the ring of C12–C17) with a centroid-to-centroid distance of 3.6845(13) Å. The existence of hydrogen bonds and face to face π – π interactions consolidate the complex **1**.

In complex **2**, coordinated water molecules in cationic motifs form hydrogen bonds with 4-sb ligands through sulfonate and carboxyl groups and these hydrogen-bonding interactions hold the cationic motifs and anions into 3-D supra-molecular assembly (Fig. 5). No any π - π stacking interaction can be found in complex **2**.



Fig. 2. ORTEP view of the molecular structure of complex 2 (a) and 1-D cationic chain (b). Symmetry code: (i) 2-x, 2-y, 2-z; (ii) 1-x, 1-y, 1-z.



Fig. 3. ORTEP view of the molecular structure of complex 3 (a) and 1-D chain (b). Symmetry code: (i) 2-x, 2-y, 1-z; (ii) 1-x, 1-y, 1-z.

Table 3	
Selected bond lengths (Å) an	d angles (°) for complex 2

Zn1-06	2.1875(15)	Zn1-07	2.1597(15)
Zn1-08	2.0977(14)	Zn1-09	2.1115(15)
Zn1-N1	2.1393(15)	Zn1-N2	2.1410(16)
06-Zn1-07	177.91(6)	06-Zn1-08	91.05(6)
06-Zn1-09	88.08(6)	06-Zn1-N1	89.47(6)
06-Zn1-N2	89.65(6)	07-Zn1-08	86.89(6)
07-Zn1-09	93.99(6)	07-Zn1-N1	90.80(6)
07-Zn1-N2	90.21(6)	08-Zn1-09	178.91(5)
08-Zn1-N1	88.91(6)	08-Zn1-N2	94.99(6)
09-Zn1-N1	90.43(6)	09-Zn1-N2	85.66(6)
N1-Zn1-N2	176.02(6)		

Table 4

Selected bond lengths (Å) and angles (°) for complex 3.

Zn1-O1 ⁱ	2.066(3)	Zn1-03	2.164(4)
Zn1-06	2.141(4)	Zn1-N1	2.148(4)
Zn1-N2	2.162(5)	Zn1-N3	2.164(4)
01 ⁱ -Zn1-03	97.17(15)	01 ⁱ -Zn1-06	91.95(14)
O1 ⁱ –Zn1–N1	168.95(17)	O1 ⁱ -Zn1-N2	93.15(15)
O1 ⁱ –Zn1–N3	89.20(14)	03-Zn1-06	88.94(17)
03-Zn1-N1	93.22(16)	03-Zn1-N2	169.27(14)
03-Zn1-N3	84.31(17)	06-Zn1-N1	84.48(14)
06-Zn1-N2	93.64(17)	06-Zn1-N3	173.24(16)
N1-Zn1-N2	76.69(16)	N1-Zn1-N3	95.57(15)
N2-Zn1-N3	92.94(17)		

Symmetry code: (i) 2-x, 2-y, 1-z.

In complex **3**, hydrogen bonds between carboxyl groups and lattice water molecules, between lattice water molecules, between sulfonate groups and lattice water molecules, and between lattice water molecules and coordinated water molecules extend the 1-D zig-zag structure into a 3-D supra-molecular assembly (Fig. 6). Offset face to face π - π interactions occur between symmetrical 2,2'bipy rings with a centroid-to-centroid distance of 3.856(3) Å.

3.4. IR spectra analysis

In these three complexes, COOH characteristic peaks near 1680 cm⁻¹ are absent, indicating that each carboxyl group for 4-sb ligands is deprotonated. The broad peaks at 3377 cm^{-1} in **1**, 3301 cm^{-1} in **2**, and 3427 cm^{-1} in **3** suggest the presence of water molecules in these three complexes. The symmetrical and unsymmetrical peaks of carboxylates are observed at 1552 and

1317 cm⁻¹ for **1**, 1545 and 1421 and 1377 cm⁻¹ for **2**, and 1551 and 1320 cm⁻¹ for **3**, respectively. The characteristic vibrations of $v_{\rm s}({\rm SO}_3^-)$ are at 1220, 1196, 1117 cm⁻¹ in **1**, 1228, 1176, 1115 cm⁻¹ in **2**, and 1229, 1183, 1162, 1119 cm⁻¹ in **3**, respectively; further $v_{\rm as}({\rm SO}_3^-)$ peaks are at 1035 cm⁻¹ in **1**, 1034 cm⁻¹ in **2**, and 1036 cm⁻¹ in **3**, respectively. The characteristic peaks of the 2,2'-bipyridine are at about 1598, 1443, and 767 cm⁻¹ in **1**, and 1609, 1446, 779 cm⁻¹ in **3**.

3.5. Thermal stability behavior

Thermal analyses of complexes 1-3 were done under a flow of nitrogen gas from room temperature to 800 °C at heating rate of 10 °C min⁻¹. TG analysis for **1** shows that three-step weight loss was observed from room temperature to 75 °C, 75-116 °C, and 117-130 °C. Total weight loss of 14.5% corresponds to the release of four water molecules (calculated 14.6%). The complex decomposed at the range 250-780 °C with the loss of 2,2'-bipy and 4-sb ligands (calculated 68%, observed 67.8%), and the residue was ZnO. For complex 2, the weight loss started at 66 °C, and in the range 66–167 °C the total loss of 14.2% corresponds to the release of four water molecules (calculated 14.6%). Complex 2 began to decompose at 285 °C and ended at 658 °C with the loss of 4,4'-bipy and 4-sb ligands (calculated 68%, observed 67%), and the residue was ZnO. Complex **3** released three water molecules from room temperature to 100 °C with the weight loss of 9.5% (calculated 9.7%) and the complex decomposed at 243 °C. Complex 2 has the higher temperature of water loss than those of complexes **1** and **3**. which is agreement with the results that lattice water molecules are easier to loss than that of coordinated water molecules.

3.6. Fluorescent emission

Complexes **1–3** have the similar fluorescent properties in solid state at room temperature ($\lambda_{ex} = 220$ nm). The maximum emission wavelengths occur at 470 nm in these three complexes. These emissions may be mainly caused by 4-sb, 2,2'-bipyridine, or/and 4,4'-bipyridine ligands by comparison with the free ligands of 2.2'-bipy, 4,4'-bipy or K(4-Hsb). And these maximum emissions in complexes **1–3** have the emission strength of **2** > **3** > **1**, furthermore these emissions are stronger than free ligands, K(4-Hsb), 2,2'-bipyridine, and 4,4'-bipyridine, indicating the coordination enhances the emission absorptions.



Fig. 4. A view of 3-D hydrogen-bonding architecture for complex 1.



Fig. 5. A view of 3-D hydrogen-bonding supra-molecular assembly for complex 2.



Fig. 6. A view of 3-D hydrogen-bonding supra-molecular assembly for complex 3.

4. Conclusions

Three Zn^{II}/4-sulfobenzoate complexes based on 2,2'-bipyridine and/or 4,4'-bipyridine ligands have been synthesized by hydro-thermal synthesis and characterized by elemental analyses, IR spectra, TG analyses, fluorescent spectra, and single-crystal X-ray

analyses. These three complexes exhibit a monomer for complex **1**, linear cationic chain in **2**, and zig-zag chain for complex **3**. In the complexes containing 2,2'-bipyridine ligands, 4-sb ligands coordinate with metal ions, while in complex **2** the 4-sb is non-coordinating. Hydrogen bonds are found in these three complexes, while π - π interactions only occur in complexes **1** and **3**. There is

no any π - π interaction between 4,4'-bipyridine ligands or 4,4'bipyridine and 4-sb ligands. These extending hydrogen-bonding supra-molecular assembles are 3-D architectures. These three diverse structures cause different properties, (1) complex **2** has the highest water loss temperature; (2) the fluorescent emission strength order is **2** > **3** > **1**.

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