

Two Chiral Coordination Polymers: Preparation and X-ray Structures of Mono(4-sulfo-L-phenylalanine)(diaqua) Zinc(II) and Copper(II) Complexes

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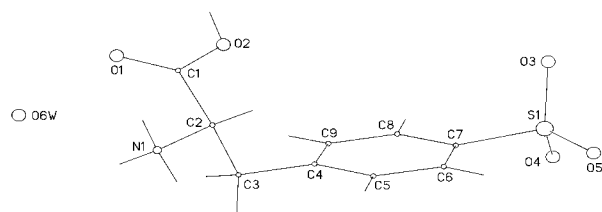
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Introduction

Helicity and chirality are of intense current interest in chemistry, biochemistry, pharmaceuticals, agrochemistry, and materials science.^{1,2} The design and preparation of chiral self-assembling systems is among the most challenging tasks of supramolecular chemistry and crystal engineering.^{3,4} Recently, chiral metal–organic coordination polymers have found wide applications in enantioselective synthesis, asymmetric catalysis, zeolites, nonlinear optical materials (second harmonic generation (SHG)), magnetic materials, and inclusion chemistry.^{5–8} Generally chiral architectures are realized through achiral building blocks or through chiral building

Scheme 1



blocks. It makes possible the rational design and synthesis of supramolecular aggregates with one-, two-, or three-dimensional networks which have chirality.⁹

Our current research is focused on the synthesis of chiral polymers to explore advanced materials for preparative-scale chiral separations, enantioselective sieves, and SHG materials. 4-Sulfo-L-phenylalanine (H₂SPA) (Scheme 1) has been used as an anticoagulant, for preparation of hydroxamic acid derivatives, as TNF-production inhibitors, and in substances for lightening skin and for preventing browning of the skin.¹⁰ Its coordination chemistry has also aroused wide attention during the past three decades. The idea behind our choice of the ligand-containing sulfonate group as a building block is that even if the metal–organic coordination polymers are multidimensional, they still can be soluble in water due to the strong hydrophilic capacity of the sulfonate group, which is very useful for organic catalytic asymmetric reactions

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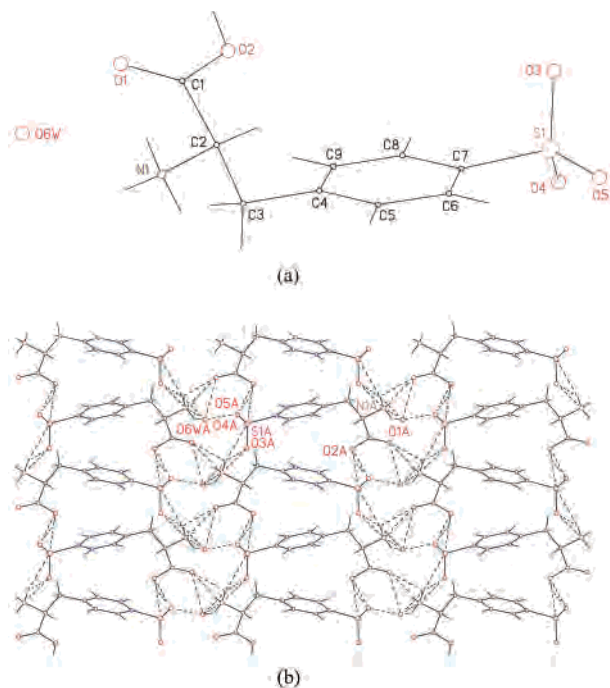


Figure 1. (a) Molecular structure of H₂SPA. (b) A crystal packing perspective view of H₂SPA. The dashed lines stand for hydrogen bonding (H atoms are omitted for clarity).

in aqueous media leading to benign chemical synthesis.¹¹ To this end, we employ H₂SPA as a chiral building block and, through hydrothermal synthesis, successfully gain two 1-D aqueous-soluble chiral metal coordination polymers [Zn(SPA)(H₂O)₂]_n (**1**) and [Cu(SPA)(H₂O)₂]_n (**2**). **1** and **2** represent the first examples of chiral metal coordination polymers with a sulfonate group having a strong SHG response in the solid state. Herein we report the preparation of **1** and **2**, their crystal structures, and the SHG properties of **1**.

Results and Discussion

The reaction of L-phenylalanine with H₂SO₄ (98%) yielded 4-sulfo-L-phenylalanine (H₂SPA). Recently both Werner¹⁰ and Parent¹² reported the synthesis and characterization of the ligand H₂SPA. We have prepared H₂SPA with a modified procedure and obtained its crystal structure (Figure 1a). It is worth noting that the sulfonic H atom has moved to amido and this zwitterionic mode of H₂SPA in acidic solution is in favor of the structure proposed by Parent.¹² To take hydrogen bonding into account, H₂SPA forms a 3-D network (Figure 1b).

Hydrothermal reactions of H₂SPA with Zn(OH)₂ and Cu(OH)₂ afforded [Zn(SPA)(H₂O)₂]_n (**1**) and [Cu(SPA)(H₂O)₂]_n (**2**), respectively. The presence of carboxylate groups in both **1** and **2** was definitely confirmed by the strong peaks at 1600, 1580, and 1440 cm⁻¹ for **1** and 1611, 1568, and 1433 cm⁻¹

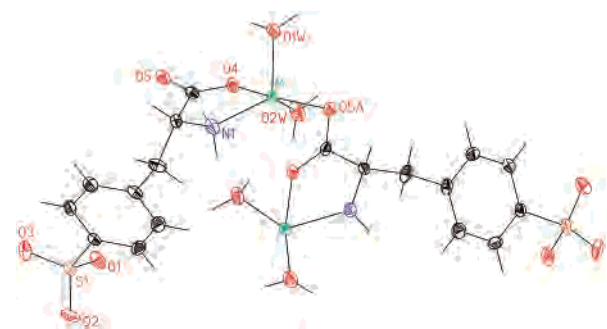


Figure 2. An ORTEP view of [M(SPA)(H₂O)₂]_n (M = Zn²⁺ (**1**) and Cu²⁺ (**2**)); thermal ellipsoids are drawn at the 30% probability level.

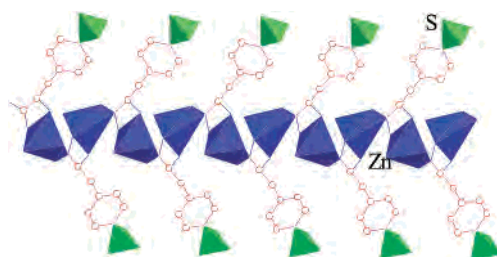


Figure 3. A 1-D chain representation of [M(SPA)(H₂O)₂]_n highlighting M trigonal bipyramid and S tetrahedron (M = Zn²⁺ (**1**) and Cu²⁺ (**2**)).

for **2** (C=O stretching mode) in their IR spectra. Moreover, the strong wide peaks at 1250–1150 cm⁻¹ indicate the existence of sulfonate groups in **1** and **2**, compared to that of free ligand H₂SPA. Both **1** and **2** are soluble in water and alcohol.

The one-dimensional polymeric structure of **1** was revealed in an X-ray single-crystal diffraction study in which the coordination environment around the Zn(II) center in **1** is a distorted trigonal bipyramid (Figure 2; **2** is isostructural to **1**). The Zn atom is approximately located in the center of the basal plane (O4–O1W–O2W) with a deviation of 0.33157 Å. The basal plane is formed by O4 and N1 atoms from the same SPA²⁻ ligand, one water molecule (O2W), and one of oxygen (O5A) of carboxylate in another SPA²⁻. The remaining apical position was occupied by one water molecule. Thus, SPA²⁻ acts as a tridentate bridging spacer to link two Zn centers, resulting in the formation of a 1-D chain, as shown in Figure 3. The salient feature in the crystal packing of **1** is that the uncoordinated O atoms of sulfonate form strong hydrogen bonding (2.747–3.239 Å) with water or amino group, resulting in the formation of a 3-D network (Figure 4). The bond distances in the carboxylate group (1.193(5)–1.301(5) Å) in the ligand H₂SPA clearly show some difference between single- and double-bond character, while almost identical bond lengths in the carboxylate in **1** (1.253(4)–1.2659(4) Å) and **2** (1.254(4) and 1.256(4) Å) were observed and are consistent with delocalization as a result of the coordination of carboxylate to metal ion. The bond distances of C–O, C–N, C–C, S–O, S–C, Zn–O, Zn–N, Cu–O, and Cu–N are unexceptional. Interestingly, no significant difference of the bond distances and angles of the uncoordinated sulfonate group was found among H₂SPA, **1**, and **2**, probably suggesting that sulfonate groups in **1** and **2** can be used as secondary supramolecular units to form supramolecular aggregates and chirality through strong

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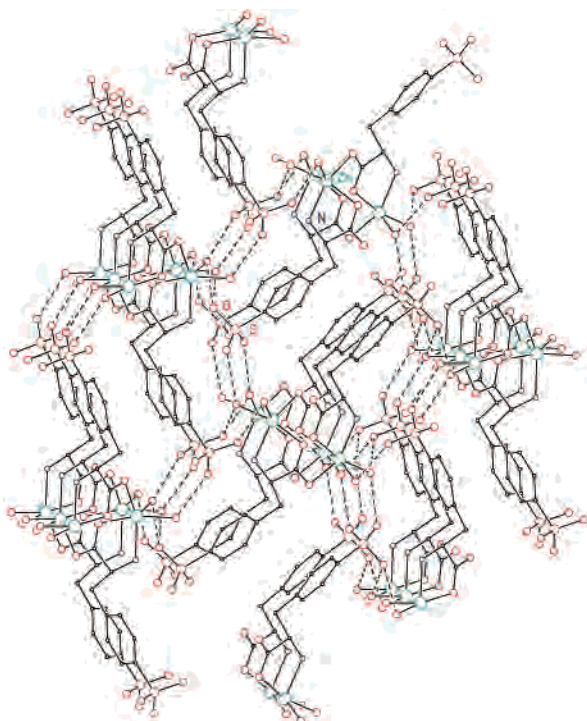


Figure 4. A crystal packing perspective view of $[M(\text{SPA})(\text{H}_2\text{O})_2]_n$ ($M = \text{Zn}^{2+}$ (**1**) and Cu^{2+} (**2**)). The open circles with increasing sizes are C, N, O, S, and M^{2+} , respectively. The dashed lines stand for hydrogen bonding (H atoms are omitted for clarity).

hydrogen bonds in their solid states. It is worth noting that the formation of strong hydrogen bonding between sulfonate groups (pure organic compound) and derivatives containing hydroxy or amino have also found wide applications in the molecular recognition.¹³ More recently, metal coordination polymers containing sulfonate direct coordination have aroused wide attention.¹⁴ However, chiral metal–organic coordination polymers containing sulfonate groups, as we are aware, still remain unknown. **1** and **2** represent the first such coordination polymers in which they possess the merit of both sulfonate compound and metal coordination polymer.

As Verbiest and a co-worker pointed out, “*strong enhancement* of nonlinear optical properties can be achieved through *supramolecular aggregates and chirality*.”¹⁵ Our experimental results indicated that the SHG response of **1** is much stronger than that of free H_2SPA ligand, and it is estimated to be about 8–10 times as high as that of H_2SPA while the relative intensity of the SHG of **1** is about similar to that of urea. Thus, the observed SHG property enhancement of **1** is probably due to sulfonate group capable of forming strong supramolecular aggregates and chirality

Table 1. Crystal Data and Structure Refinement for H_2SPA , **1**, and **2**

	H_2SPA	1	2
empirical formula	$\text{C}_9\text{H}_{13}\text{NO}_6\text{S}$	$\text{C}_9\text{H}_{13}\text{NO}_7\text{SZn}$	$\text{C}_9\text{H}_{13}\text{NO}_7\text{SCu}$
fw	263.26	344.63	342.00
T , K	293(2)	293(2)	293(2)
cryst syst	monoclinic	orthorhombic	orthorhombic
space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
a , Å	6.5297(9)	6.3656(2)	6.2058(8)
b , Å	7.6212(15)	11.6782(3)	11.4263(15)
c , Å	11.6114(14)	16.9190(9)	17.959(2)
α , deg	90.00	90.00	90.00
β , deg	93.637(10)	90.00	90.00
γ , deg	90.00	90.00	90.00
V , Å ³	576.67(16)	1257.74(6)	1273.5(3)
Z	2	4	4
ρ (calcd), g/cm ³	1.516	1.820	1.788
μ (Mo $K\alpha$), cm ⁻¹	2.98	21.470	19.070
$F(000)$	276	704	700
GOF	1.008	0.967	0.919
$R1, wR2^a$			
$I > 2\sigma(I)$	0.0427, 0.1023	0.0396, 0.0831	0.0375, 0.0831
all data	0.0625, 0.1129	0.0544, 0.0880	0.0443, 0.0853

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

through H bonds. At the same time, a sulfonate group in a ligand can be considered a good acceptor to enhance the SHG response. On the other hand, it is interesting to note that strong hydrogen bonding in compound **1** further supports the fact that hydrogen bonding can be considered as a donor–acceptor system which can significantly enhance the SHG response or be a very useful second way of linking donor and acceptor, because hyperpolarizabilities strongly depend on the number molecules aggregated through H bonds.¹⁶ Also it is interesting to see that the SHG response of powder L-phenylalanine (without a sulfonate group) is weaker than that of H_2SPA , while the SHG response of powder bis(L-phenylalaninato)zinc(II) is also significantly weaker than that of **1** in about 4–6 times. This is why the introduction of a sulfonate group into L-phenylalanine leads to the significant enhancement of the SHG response in H_2SPA and **1**.

In conclusion, the combination of chiral metal–organic coordination polymer and sulfonate group displays the capacity of the formation of strong supramolecular aggregate and chirality through H bonds and represents a *new strategy* to design *SHG* materials.

Experimental Section

Preparation of H_2SPA . The ligand H_2SPA was prepared by a modified published procedure.¹² L-Phenylalanine (15 g, 0.091 mol) and sulfuric acid (98%, 25 mL) were stirred for 2.5 h in an oil bath at 170 °C. After addition of 40 mL of H_2O at 0 °C, precipitation occurred and the precipitate was filtered off and recrystallized from

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NOTE

Table 2. Selected Bond Distances (Å) and Angles (deg) in H₂SPA, **1**, and **2**

H ₂ SPA		1		2	
Distances (Å)					
S(1)–O(5)	1.435(4)	Zn(1)–O(5)	2.010(3)	Cu(1)–O(5)	1.944(2)
S(1)–O(4)	1.454(3)	Zn(1)–O(1w)	2.072(3)	Cu(1)–O(2w)	1.965(3)
S(1)–O(3)	1.455(4)	Zn(1)–O(2w)	2.071(3)	Cu(1)–O(1)	1.982(2)
S(1)–C(7)	1.768(4)	Zn(1)–N(1)	2.076(3)	Cu(1)–N(1)	1.944(3)
C(1)–O(1)	1.193(5)	Zn(1)–O(4)	2.098(3)	Cu(1)–O(1w)	2.228(3)
C(1)–O(2)	1.301(5)	S(1)–O(1)	1.470(3)	S(1)–O(2)	1.438(3)
C(2)–N(2)	1.482(5)	S(1)–O(3)	1.452(3)	S(1)–O(3)	1.445(3)
		S(1)–O(2)	1.448(3)	S(1)–O(4)	1.461(3)
		S(1)–C(4)	1.764(4)	S(1)–C(7)	1.772(4)
		C(9)–O(4)	1.253(4)	C(9)–O(5)	1.254(4)
		C(9)–O(5)	1.265(4)	C(9)–O(1)	1.256(4)
		C(8)–N(1)	1.470(5)	C(8)–N(1)	1.472(5)
Angles (deg)					
O(5)–S(1)–O(4)	113.5(3)	O(5)–Zn(1)–O(1w)	103.59(12)	O(5)–Cu(1)–O(2w)	167.94(11)
O(5)–S(1)–O(3)	113.3(3)	O(5)–Zn(1)–O(2w)	95.09(12)	O(5)–Cu(1)–O(1)	91.02(10)
O(4)–S(1)–O(3)	109.4(3)	O(1w)–Zn(1)–O(2w)	93.36(13)	O(2w)–Cu(1)–O(1)	89.32(11)
O(5)–S(1)–C(7)	107.6(2)	O(1w)–Zn(1)–N(1)	113.00(13)	O(5)–Cu(1)–N(1)	82.53(11)
O(4)–S(1)–C(7)	106.7(2)	O(2w)–Zn(1)–N(3)	87.40(11)	O(2w)–Cu(1)–N(1)	93.97(12)
O(3)–S(1)–C(7)	105.8(2)	O(5)–Zn(1)–O(4)	96.90(11)	O(1)–Cu(1)–N(1)	164.00(12)
O(1)–C(1)–O(2)	126.2(4)	O(1w)–Zn(1)–O(4)	88.49(12)	O(5)–Cu(1)–O(1w)	101.01(12)
N(1)–C(2)–C(1)	107.4(3)	O(2w)–Zn(1)–O(4)	167.08(10)	O(2w)–Cu(1)–O(1w)	90.89(13)
N(1)–C(2)–C(3)	110.8(4)	N(1)–Zn(1)–O(4)	80.13(11)	O(1)–Cu(1)–O(1w)	97.69(12)
		O(2)–S(1)–O(3)	114.43(18)	O(2)–S(1)–O(3)	114.5(2)
		O(2)–S(1)–O(1)	110.8(2)	O(2)–S(1)–O(4)	110.2(2)
		O(3)–S(1)–O(1)	110.78(18)	O(4)–S(1)–O(3)	112.00(19)

80% ethyl alcohol/H₂O, yielding 14.6 g (61%) of large rhomboid crystals of S-4-sulfophenylalanine (H₂SPA). Found: C 40.02; H 4.94; N 5.32. Calcd: C 39.95; H 4.82; N 5.50. IR (KBr, cm⁻¹): 3700 (m), 3400 (s), 1800 (s), 1690 (m), 1580 (m), 1500 (w), 1460 (w), 1250 (s), 1180 (s), 1100 (m), 1070 (m), 900 (m), 760 (m), 680 (m).

Preparation of [Zn(SPA)(H₂O)₂]_n (1**).** A heavy-walled Pyrex tube containing a mixture of Zn(OH)₂ (0.0199 g, 0.2 mmol), H₂SPA (0.0491 g, 0.2 mmol), and H₂O (0.8 mL) was frozen in liquid nitrogen, sealed under vacuum, and placed inside of an oven at 120 °C. Colorless block crystals (0.0283 g, 41% yield based on Zn(OH)₂) were harvested in 24 h. Found: C 31.34; H 3.77; N 4.06. Calcd: C 31.42; H 3.82; N 4.14. IR (KBr, cm⁻¹): 3340 (s), 1600 (s), 1572 (m), 1438 (m), 1221 (s), 1165 (s), 1123 (m), 1069 (m), 1036 (m), 1090 (m), 820 (m), 703 (m), 601 (m), 554 (m).

Preparation of [Cu(SPA)(H₂O)₂]_n (2**).** The procedure is similar to that used in the preparation of **1** except that Cu(OH)₂ was used. Blue block crystals (61% yield based on Cu(OH)₂) were harvested after heating for 24 h. Found: C 31.38; H 3.67; N 4.15. Calcd: C 31.58; H 3.80; N 4.09. IR (KBr, cm⁻¹): 3432 (s), 3317 (s), 3275 (s), 1611 (s), 1568 (m), 1433 (m), 1294 (s), 1179 (s), 1123 (s), 1038 (m), 1011 (m), 851 (m), 709 (m), 681 (m), 589 (m).

X-ray Crystallographic Determinations of Ligand H₂SPA, **1, and **2**.** Data were collected at room temperature using epoxy-coated crystals mounted on glass fiber. All measurements were made on a Smart CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å), except that data of H₂SPA was performed on an Enraf-Nonius CAD4 diffractometer. Empirical absorption corrections were applied in each case.¹⁷ The relevant crystallographic data are presented in Table 1 while the selected bond lengths and angles are given Table 2. The structures were solved with direct methods using the program SHELXTL (Sheldrick, 1997).¹⁸ All the non-hydrogen atoms were located from the

trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedures. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The final difference Fourier map was found to be featureless.

The SHG Measurement of Ligand H₂SPA and **1.** The SHG responses of H₂SPA and **1** were estimated by measuring a powder sample (ca. 80–120 μ m in diameter, Kurtz powder test¹⁹), relative to urea. A pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate a SHG signal from samples. The emission green light (532 nm) was estimated for intensity. The SHG efficiency of H₂SPA and **1** is estimated to be approximately 0.1 and 1.0 times of that of urea, respectively.

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Supporting Information Available: Tables of bond distances, bond angles, anisotropic temperature factor parameters, and atomic coordinates for H₂SPA, **1**, and **2** and crystallographic information in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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