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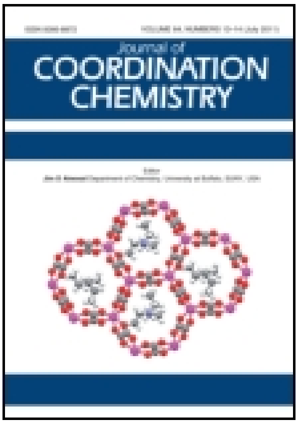

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Ag(I) coordination polymer with pyrazine sulfonic acid: synthesis, crystal structure, and fluorescence property

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Ag(I) coordination polymer with pyrazine sulfonic acid: synthesis, crystal structure, and fluorescence property

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A one-dimensional rigid, linear Ag(I) coordination polymer with pyrazine sulfonic acid, $[Ag_2L_2 \cdot H_2O]_n$ (L = pyrazine sulfonic acid) has been synthesized and characterized by elemental analyses, infrared spectroscopy, thermogravimetric analysis, and X-ray crystallography. The structure determination shows Ag(I) centers linked by bridging pyrazine ligands to give a double-chain structure sustained by weak Ag-O and Ag-N interactions. The sulfonate and pyrazine are all involved in hydrogen bonding interaction. The interactions combine with weak π-π stacking to play deciding roles defining the supramolecular structures. A powder X-ray diffraction study implies good phase purity. Solid-state fluorescence quenching and thermal stability are also discussed.

Keywords: Ag(I) coordination polymer; Pyrazine sulfonic acid; Crystal structure; Fluorescence analysis

1. Introduction

There has been much controversy concerning transition-metal complexes with heterocyclic sulfonates, which stems from the alkalescence of sulfonates and, hence, expected poor coordinating ability to transition-metal ions [1–6]. However, in recent years, sulfonates have been extensively synthesized and investigated for: (i) fascinating structural topologies and (ii) formation of inorganic – organic lamellar structures, (iii) flexible coordination modes, (iv) interesting bioactivities, and abilities to (v) intercalate guest molecules for use in metal-organic frameworks (MOF) [7–14]. Ag(I) sulfonates are most representative, as in heterocyclic sulfonate complexes described by Shimizu [15].

Herein, work to understand effects of the organic group on the structures of Ag(I) sulfonates has been investigated [16–20]. Coordination numbers from two to eight have been reported. Materials with higher coordination numbers between five and eight form less than 5% of the crystallographically characterized Ag(I) complexes and have been

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summarized in a recent review [21]. Thus far, investigation of metal sulfonates with different heterocyclic N-containing ligands is insufficient. Furthermore, there is little information available about pyrazine sulfonic acid as a ligand to synthesize complexes with transition-metal ions.

Our group also has interest in heterocyclic sulfonate-coordinated transition-metal complexes [22–27]. We report in this article a one-dimensional (1D) rigid, linear Ag(I) polymer, $[Ag_2L_2 \cdot H_2O]_n$ (L = pyrazine sulfonic acid), along with the thermal stability and luminescent properties.

2. Experimental

2.1. *Materials and methods*

All reagents and solvents used for synthesis and analysis were of analytical grade and used without purification. The ligand was obtained according to the literature [28]. To a methanol solution of pyrazine sulfonic acid (0.3 mmol) was added an aqueous suspension of $AgNO_3$ (0.4 mmol). The mixture was kept in the dark, stirred at 70°C for 8 h and then filtered. Colorless needles were obtained by evaporating the resulting clear solution slowly for 35 days at room temperature. Yield 20.3% (based on Ag). Anal. Calcd for $C_8H_8Ag_2N_4O_7S_2$ (%): C, 17.41; H, 1.46; N, 10.15. Found: C, 18.26; H, 1.39; N, 10.08. IR (cm^{-1}): 3413(m), 1457(w), 1407(w), 1388(m), 1237(vs), 1211(vs), 1181(m), 1151(m), 1053(m), 103(s), 1019(m), 864(m), 7715(m), 644(s), and 480(s).

2.2. *X-ray crystallography*

Diffraction intensities were collected on a Bruker Apex CCD area-detector diffractometer (Mo–Kα, $\lambda = 0.71073$ Å) at 293 K. The structure was solved with direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package [29]. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogens were generated geometrically. Crystallographic data for polymer is summarized in table 1. Selected bond distances and angles are listed in table 2.

3. Results and discussion

3.1. *Description of structure*

A single-crystal X-ray crystallographic study revealed the solid to consist of a linear polymeric 1D chain with two different Ag(I) ions present (figure 1). Ag(1) shows a distorted tetrahedral geometry, coordinated by two nitrogens and two oxygens. Ag(2) is coordinated by two nitrogens from two bridging pyrazine sulfonic acid ligands (N(2)-Ag(2)-N(4) 152°) in an approximately linear geometry. The bond distances of (Ag1-N1 2.281(4) Å) and (Ag1-N3 2.220 Å) are shorter than those reported previously [30] while the (Ag1-O1C 2.569(5) Å) and (Ag1-O7 2.480(6) Å) are longer [31]. Water coordinated to Ag(1) with three nearby ligands forms a basal plane

Table 1. Crystal data and structure refinements for $[Ag_2L_2 \cdot H_2O]_n$.

Empirical formula	$C_8H_8Ag_2N_4O_7S_2$
Formula weight	552.06
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions (Å, °)	
a	15.731(3)
b	14.165(3)
c	14.395(3)
α	90.00
β	121.62(3)
γ	90.00
Volume (Å^3), Z	2731.5(13), 8
D_c (g cm^{-3})	2.685
F (000)	2040
θ range for data collection (°)	3.04–25.24
Reflections collected	7947
Independent reflection	2468 [R(int) = 0.0392]
Goodness-of-fit on F^2	1.013
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0437$, $wR_2 = 0.1050$
R indices (all data)	$R_1 = 0.0501$, $wR_2 = 0.1094$

Table 2. Selected bond distances (Å) and angles (°) for $[Ag_2L_2 \cdot H_2O]_n$.

Bond distances (Å)			
Ag1–O1A	2.569(4)	Ag1–O7	2.485(5)
Ag1–N1	2.280(4)	Ag1–N3	2.220(4)
Ag2–N2	2.260(4)	Ag2–N4B	2.277(4)
Bond angles (°)			
N3–Ag1–N1	152.90(17)	N3–Ag1–O7	115.13(17)
N1–Ag1–O7	91.02(16)	N3–Ag1–O1A	98.87(15)
N1–Ag1–O1A	89.04(14)	O7–Ag1–O1A	86.91(17)
N2–Ag2–N4B	151.57(17)		

Symmetry codes: A $-x+1$, y, $1/2-z$; B x, $1+y$, z.

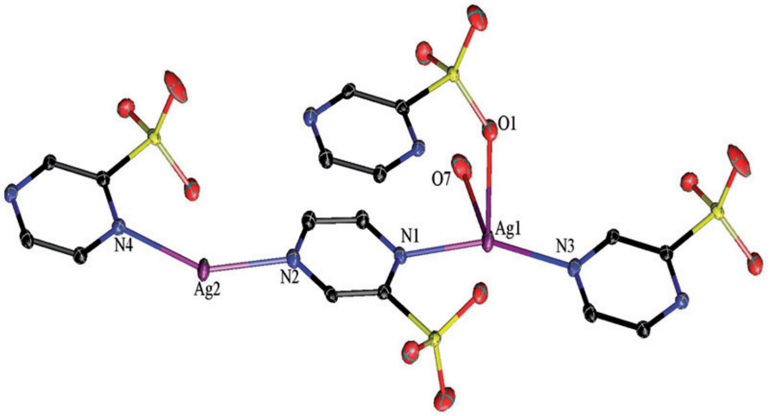

Figure 1. Coordination environments of Ag(I) ions.

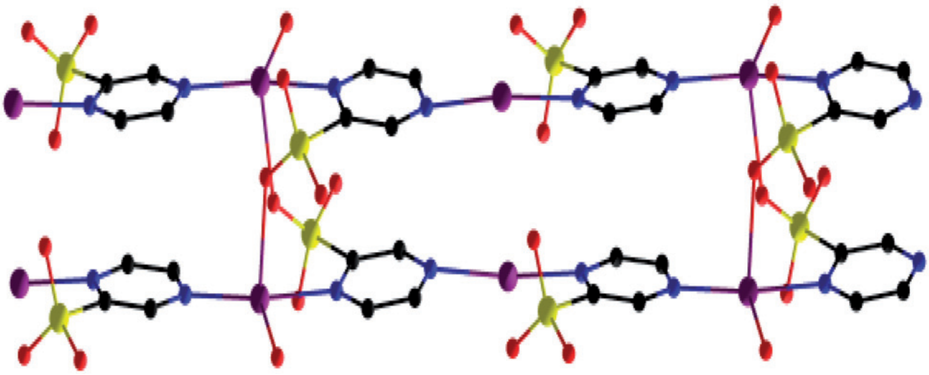

Figure 2. 1D double-chain of polymer.

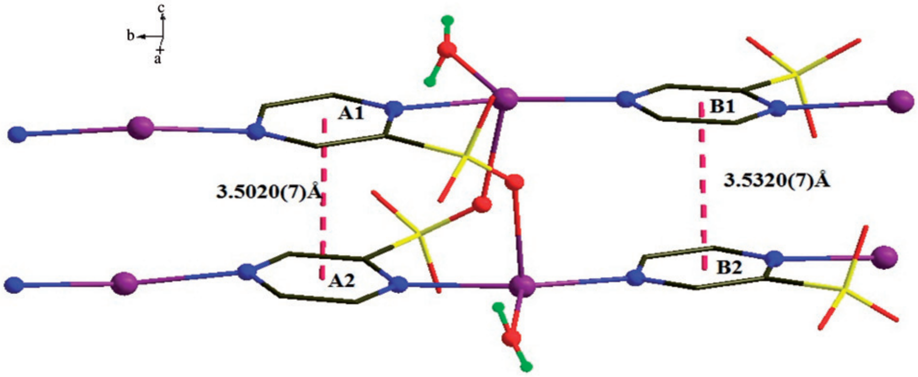

Figure 3. Distance of centroid-to-centroid of pyrazine rings and π-π interactions.

(N(1)-Ag(1)-O(7) 91.22°, O(7)-Ag(1)-N(3) 114.9° and N(1)-Ag(1)-N(3) 152.9°). Three Ag ions are bridged by one ligand to construct an infinite double-chain in the equatorial direction (figure 2). From the crystal packing of the polymer, the pyrazines are parallel to each other in the double-chain with a centroid-to-centroid distance of 3.46 Å, which supports the presence of π–π stacking interactions. The assembly can be regarded as a 2D layer sustained by the weak forces (figure 3). The coordinated waters and sulfonic acid groups participate in O–H $\cdots$ O and C–H $\cdots$ O hydrogen bonds (table 3), which define a 3D hydrogen-bonded network and, thus, support the supramolecular architecture [32, 33] (figure 4).

3.2. *Powder X-ray diffraction analysis*

The result of PXRD diffraction analysis reveals all peaks of both simulated and experimental patterns that match in relevant positions, thus, suggesting bulk phase purity of the polymer (figure 5).

Table 3. Selected hydrogen-bond geometries (Å) for $[Ag_2L_2 \cdot H_2O]_n$.

D–H···A	D–H	H···A	D···A	D–H···A
O7–H7A···O3#2	0.83	2.58	3.384(8)	165
O7–H7B···O2#3	0.82	2.18	2.904(7)	147
O7–H7B···O5#4	0.82	2.28	2.817(9)	123
C1–H1···O7	0.93	2.57	3.274(8)	133
C1–H1···O3#5	0.93	2.49	3.088(8)	122
C2–H2···O6#1	0.93	2.36	3.159(7)	143
C2–H2···O3#5	0.93	2.45	3.067(8)	124
C3–H3···O3	0.93	2.53	2.886(7)	103
C3–H3···O7#6	0.93	2.52	3.365(8)	150
C5–H5···O1	0.93	2.47	3.182(7)	133
C5–H5···O4#	0.93	2.45	3.040(8)	121
C6–H6···O2#8	0.93	2.60	3.238(8)	127
C6–H6···O4#7	0.93	2.48	3.056(7)	120
C8–H8···O4	0.93	2.52	2.882(7)	104

Symmetry codes: #1 $x, 1+y, z$; #2 $1-x, -y, -z$; #3 $3/2+x, 3/2+y, z$; #4 $1/2-x, 1/2+y, 1/2-z$; #5 $-1/2+x, 3/2-y, -1/2+z$; #6 $1/2+x, 3/2-y, 1/2+z$; #7 $1/2+x, 1/2-y, 1/2+z$; #8 $1+x, -1-y, -1/2+z$.

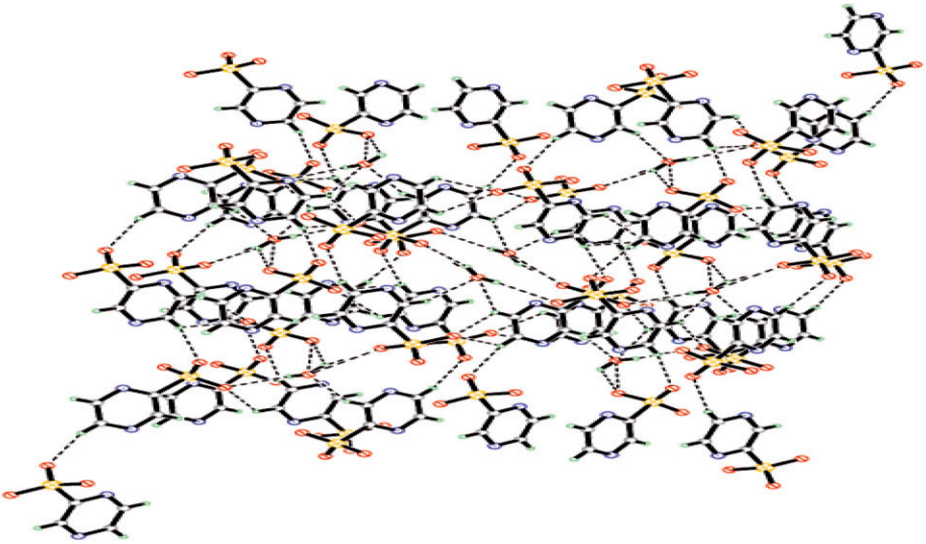

Figure 4. Hydrogen bonds that make up a 3D network polymer.

3.3. *Luminescence*

The luminescent properties of metal complexes with pyrazine sulfonates are rarely explored, even though many Ag(I) sulfonates have been reported. Consequently, the luminescences of the title polymer, as well as the free ligand, were examined at room temperature in the solid state. The free ligand exhibits strong energy absorption from 320 to 380 nm with a blue fluorescence emission band at 400 nm. The resulting polymer did not exhibit luminescence, possibly owing to a heavy atom effect that involves the coordination of the ligand to Ag(I) [34–37].

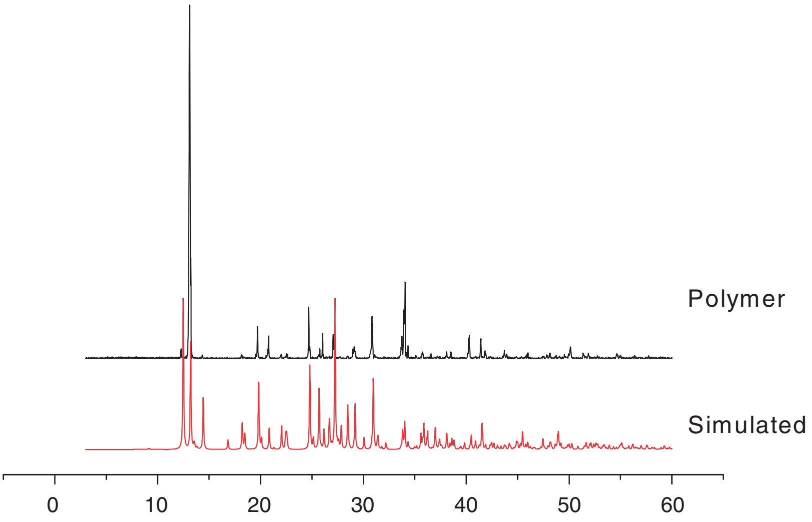

Figure 5. X-ray powder diffraction (XPD) pattern of $[Ag_2L_2 \cdot H_2O]_n$.

3.4. *Thermal analysis*

The thermal behavior of the polymer was examined by thermogravimetric analysis (TGA; Supplementary material). In particular, three steps of weight loss were observed in the curve. A weight loss related to gradual release of coordinated water was observed from room temperture to 120°C (Obs. 3.9%, Calcd 3.3%). The framework appeared to remain stable up to 378°C. Rapid decomposition of the polymer began at 380°C, with the temperature range 380 to 426°C assumed as the loss of the ligand (Obs. 45.86%, Calcd 45.23%). Complete decomposition did not occur until 945°C (Obs. 60.1%, Calcd 59.6%).

Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center with CCDC deposition numbers 825573 for $[Ag_2L_2 \cdot H_2O]_n$ (L = pyrazine sulfonic acid). Copies of this information may be obtained free of charge from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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