

Articles

# Luminescent Property of a Supramolecular Silver(I)-Thiolate Complex Based on Secondary Ag-S Interactions and Hydrogen Bonds

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The supramolecular silver(I)-thiolate complex  $[\text{Ag}(\mu_2\text{-SC}_4\text{N}_2\text{H}_4)_2(\text{SCN})]_n$  has been prepared from the reaction of AgSCN and pyrimidine-2-thiol in DMF. X-ray diffraction analysis shows that the supramolecular structure exhibits one-dimensional chain through the secondary Ag-S interactions and the chains are further linked by strong hydrogen bonds to form a three dimensional network. The luminescence effect from the silver-centered state of  $\text{S} \rightarrow \text{Ag}$  LMCT in solid state is different from that in solution due to the secondary Ag-S interactions.

**Keywords** Silver(I)-thiolate, crystal structure, luminescence property

## Introduction

Supramolecular chemistry is a research area of rapid growth in recent years.<sup>1-7</sup> Much work has centered upon: (1) the uses of polypyridyl or pyrazines as exo-bidentate ligands generating oligomeric and polymeric metal complexes;<sup>3-8</sup> (2) the uses of organic synthons with both strong hydrogen bond donor and acceptor systems connecting themselves through hydrogen bonds to form infinite chain and two- or three-dimensional networks;<sup>1,9</sup> (3) understanding the course of self-assembly process. However, few researches have been reported on their physical properties and application in materials. Poly-

meric neutral metal-thiolate  $[\text{MSR}]_n$  complexes with two- or three-dimensional network are not well investigated because of their poor solubility and difficulty to obtain single crystals suitable for X-ray diffraction.<sup>10-13</sup> Recently, Parish and co-workers reported two polymeric copper-thiolate complexes from the reaction of CuCl with cysteamine hydrochloride ( $\text{HSCH}_2\text{CH}_2\text{NH}_3^+\text{Cl}^-$ ),<sup>14</sup> in which the zwitterion  $^-\text{SCH}_2\text{CH}_2\text{NH}_3^+$  acts as a neutral ligand. By introducing the zwitterion method into silver-thiolate system, we have obtained a series of polymeric complexes, such as  $(\text{Ag}_6\text{SPy}_6)_n$ ,  $(\text{AgClSPyH})_n$ <sup>15</sup> and  $\{[\text{Ag}_6\text{Cl}_6(\text{SCH}_2\text{CH}_2\text{NH}_3)_6\text{Cl}_2]\}_n$ <sup>16</sup> (SPy = pyridine-2-thiolate, SpyH = 1-H-pyridine-2-thione) from the reactions of solid silver chloride or silver salt with thiolates containing N donors. As a result of continuing interest in this class of ligands, our research has been carried out on the coordination chemistry of hydrogen-pyrimidine-2-thione, which possesses both strong hydrogen bond donor and acceptor systems. It is found that its supramolecular silver(I)-complex has strong luminescent effect both in solution and in solid. Herein we report the synthesis, crystal structure and luminescent properties of a new polymeric silver(I) complex with supramolecular structure in three-dimensional network  $[\text{Ag}(\text{Hpymt})_2(\text{SCN})]_n$  (Hpymt = 1-H-pyrimidine-2-thione) based on secondary Ag-S interactions and hydrogen bonds.

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## Experimental

All syntheses and manipulations were performed in air. The solvents used are AR reagents. Reagents pyrimidine-2-thiol and AgSCN were purchased from Aldrich Company and used without further purification.

### Preparation of complex $[\text{Ag}(\text{SC}_4\text{N}_2\text{H}_3)_2(\text{SCN})]$ (1)

A solid of AgSCN (84.0 mg, 0.50 mmol) and pyrimidine-2-thiol (110 mg, 1.0 mmol) were dissolved in DMF (25 mL). After the reaction mixture was stirred for 24 h, the solution turned clear. Upon filtration, a slow diffusion of ether into the filtrate resulted in the formation of a large amount of pale-yellow needle-crystals of the complex. After one week, yellow crystals of  $[\text{Ag}(\text{SC}_4\text{N}_2\text{H}_3)_2(\text{SCN})]$  suitable for X-ray crystallographic analysis were collected and washed with acetone and  $\text{Et}_2\text{O}$ , yield 0.11 g (33.3%). Anal. Calcd for  $\text{C}_9\text{H}_8\text{N}_5\text{AgS}_3$ ; C, 27.7; H, 2.07; N, 18.0. Found: C, 27.6; H, 2.05; N, 18.2.

### Physical measurements

Infrared spectra were recorded on an FTS-40 spectrophotometer with the use of pressed KBr pellets. Electronic absorption spectra were obtained in MeOH solution on a Shimadzu UV-3000 spectrophotometer and steady-state emission spectra on a Shimadzu RF-540 spectrofluorometer. The  $^1\text{H}$  NMR spectra were measured on a Varian Unity-500 spectrometer at 20°C in  $(\text{CD}_3)_2\text{SO}$  with TMS as standard. All elemental analyses were carried out on a Perkin-Elmer model 240C automatic instrument.

### Crystal structure determination

Single crystals for the complex were carefully chosen, coated with epoxy resin and mounted on glass fibers. Cell dimension measurements and data collections were performed on a Siemens Smart CCD diffractometer with graphite-monochromitized  $\text{Mo K}_\alpha$  radiation at  $23 \pm 1^\circ\text{C}$ . Intensity data were obtained in the range  $3.5 < 2\theta < 50.9^\circ$  by using an  $\omega$  scan technique. The data reductions were performed on a silicon graphics computer station with Smart CCD software. The coordinates of Ag, S, N and C atoms were obtained from an E-map. Suc-

cessive difference Fourier syntheses gave all the coordinates of the hydrogen atoms. The structure was refined by full matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. All calculations were performed on an HP 586 computer by using the SHELXTL PC version 5.10 program package. Crystallographic data and selected bond lengths and angles are listed in Table 1—3.

**Table 1** Crystal data, data collection and structure refinement parameters for  $[\text{Ag}(\text{SC}_4\text{N}_2\text{H}_4)_2(\text{SCN})]_n$

Empirical formula	$\text{C}_9\text{H}_8\text{N}_5\text{AgS}_3$
<i>FW</i>	388.9
Space group	$C_c$
<i>a</i> (nm)	1.6621(3)
<i>b</i> (nm)	1.0670(3)
<i>c</i> (nm)	0.7474(3)
$\beta$ ( $^\circ$ )	90.69(2)
<i>V</i> ( $\text{nm}^3$ )	1.3253(8)
<i>Z</i>	4
$\rho$ ( $\text{Mg}/\text{m}^3$ )	1.956
$\lambda$ ( $\text{mm}^{-1}$ )	1.979
<i>T</i> (K)	293
$\lambda$ (nm, Mo $K_\alpha$ )	0.071073
Observed reflections	2873 ( $F = 2.0\sigma(F)$ )
Goodness-of-fit on $F^2$	1.006
$R^a$	0.029
$R_w^b$	0.034
$\Delta\rho$ ( $\text{e}/\text{nm}^3$ )	233, -523

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; \quad ^b R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^2]^{1/2}.$$

## Results and discussion

### Synthesis and property

By the reaction of pyrimidine-2-thiol and AgSCN in a ratio of 2:1 in DMF, a large amount of colorless needle-crystal product was isolated from slow diffusion of ether into the reaction solution. The infrared spectra of the crystalline product exhibit an unresolved band in rang from 2798 to 3162  $\text{cm}^{-1}$ , which may be attributed to stretching frequencies of C—H and N—H.

### Crystal structure of compound 1

The crystallographic analysis reveals that the com-

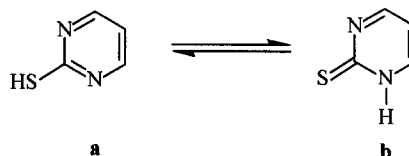
**Table 2** Atomic coordinates [ $\times 10^4$ ] and equivalent isotropic displacement parameters [ $\text{nm}^2 \times 10$ ] for  $[\text{Ag}(\text{SC}_4\text{N}_2\text{H}_4)_2(\text{SCN})]_n$ 

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq.)
Ag	8752(1)	9358(1)	3722(1)	83(1)
S	8650(1)	6954(1)	3645(4)	57(1)
S(1)	7643(1)	10375(2)	1894(2)	49(1)
S(2)	9943(1)	10206(2)	5443(2)	49(1)
N	10168(4)	6370(5)	2302(10)	69(2)
N(1)	6739(3)	12260(6)	2966(8)	50(1)
N(2)	8108(3)	12483(5)	3548(8)	47(1)
N(3)	9794(3)	12220(5)	3360(8)	43(1)
N(4)	11097(3)	11685(6)	4232(9)	49(1)
C	9540(4)	6619(5)	2865(9)	49(2)
C(1)	7501(3)	11785(5)	2895(9)	38(1)
C(2)	6582(4)	13404(8)	3620(11)	62(2)
C(3)	7192(5)	14125(7)	4276(12)	66(2)
C(4)	7960(4)	13613(6)	4236(10)	56(2)
C(5)	10305(3)	11444(5)	4268(9)	39(1)
C(6)	10039(4)	13218(6)	2427(10)	51(2)
C(7)	10838(4)	13447(7)	2367(12)	59(2)
C(8)	11345(4)	12674(7)	3293(11)	55(2)

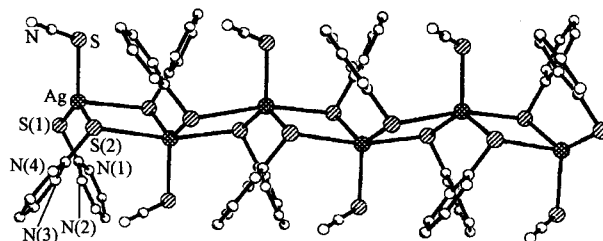
**Table 3** Bond lengths [0.1 nm] and angles [ $^\circ$ ] for  $[\text{Ag}(\text{SC}_4\text{N}_2\text{H}_4)_2(\text{SCN})]_n$ 

Ag—S	2.570(2)	Ag—S(2) #	3.203(2)
Ag—S(1)	2.527(2)	S—C	1.636(7)
Ag—S(2)	2.516(2)	S(1)—C(1)	1.698(6)
Ag—S(1) #	3.034(2)	S(2)—C(5)	1.699(6)
S(1)-Ag-S	111.65(8)	C-S-Ag	99.6(2)
S(2)-Ag-S	114.96(8)	C(1)-S(1)-Ag	104.3(2)
S(2)-Ag-S(1)	133.33(5)	C(5)-S(2)-Ag	107.2(2)

plex **1** is a supramolecular structure, in which  $[\text{Ag}(\text{Hpymt})_2(\text{SCN})]$  constitutes the basic unit. Obviously, during the process of the reaction migration of hydrogen from mecapto-group to nitrogen at pyrimidine ring led to the formation of thione ligand (**b** in scheme 1), which carries both strong hydrogen bond donor and acceptor systems and is an ideal synthon for supramolecular construction. The basic units,  $[\text{Ag}(\text{Hpymt})_2(\text{SCN})]$ , are linked by Ag-S interactions to form a one-dimensional chain structure (Fig. 1), and the chains are further linked together to yield a three-dimensional network supramolecular structure through two kinds of hydrogen bonds, the normal hydrogen bonds of  $\text{N}-\text{H}\cdots\text{N}$  between H atom at the N atom of Hpymt and N atom of SCN lig-

**Scheme 1**

and and the charge-assisted hydrogen bonds  $\text{C}-\text{H}^{\delta+}\cdots\text{N}^{\delta-}$  between H atom at the C atom of Hpymt ring and N atom of another Hpymt ring. Fig. 2 shows how the chains are connected by the hydrogen bonds to form the supramolecular structure, which is completely different from the three dimensional network structure with tetragonal channels of  $[\text{Ag}(\text{HPy})\text{Cl}]_n$ .<sup>15</sup> There are two sets of  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bonds in the supramolecular struc-

**Fig. 1** Perspective view of the unit in the polymeric complex  $[\text{Ag}(\mu_2\text{-SC}_4\text{N}_2\text{H}_4)_2(\text{SCN})]_n$ .

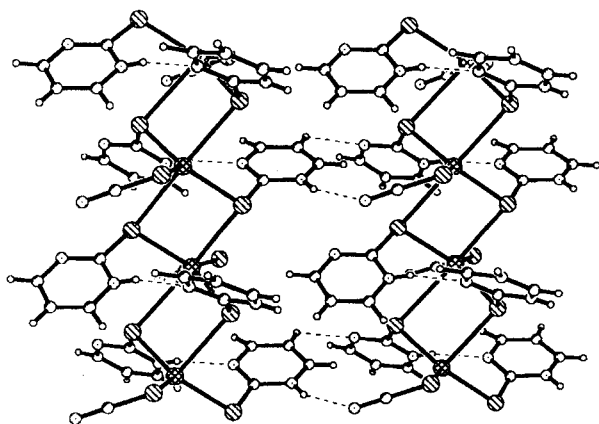


Fig. 2 View of the three-dimensional network, running along *b* axis in  $[\text{Ag}(\mu_2\text{-SC}_4\text{N}_2\text{H}_4)_2(\text{SCN})]_n$ .

ture (Fig. 3), intramolecular hydrogen bond  $\text{N}\cdots\text{N}$  distance is 0.2811 (nm) and intermolecular hydrogen bond  $\text{N}\cdots\text{N}$  distance is 0.2822 (nm). The  $(\text{C})\text{H}\cdots\text{N}$  distance is 0.2506 nm, which is compatible to those in  $\text{C}-\text{H}^{\delta+}\cdots\text{F}^{\delta-}$  and  $\text{C}-\text{H}^{\delta+}\cdots\text{O}^{\delta-}$ .<sup>2,6</sup>

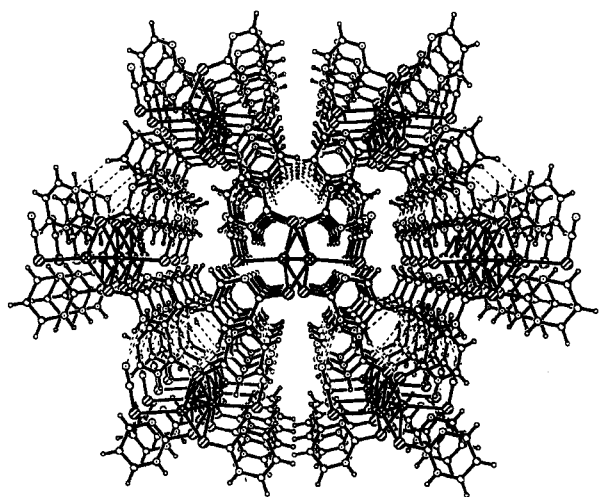


Fig. 3 Intramolecular and intermolecular hydrogen bonds in the supramolecular structure.

Each silver atom is pentacoordinated in a highly distorted trigonal bipyramid fashion of  $\text{AgS}_5$  with two sulfur atoms at the up and bottom apexes and three in the equatorial plane. Thus, each  $\text{SCN}^-$  anion acts as terminal ligand with sulfur atom coordinated and each S atom in PymtH molecule exhibits a bridge coordination mode bridging two metal centers. The three  $\text{Ag}-\text{S}$  bonds in the equatorial plane are all similar in length (0.2516

(2), 0.2527(2), and 0.2570(2) nm, while those in the apexes are quite long and nonequivalent, one at 0.3034(2) nm, the other at 0.3203(2) nm, which may be considered as a secondary  $\text{Ag}\cdots\text{S}$  interactions.<sup>17</sup> In other words, it can be viewed that the  $[\text{Ag}(\text{Hpymt})_2(\text{SCN})]$  units form chains through  $\text{Ag}\cdots\text{S}$  secondary interactions and the chains form the supramolecular network structure through hydrogen bonds. The bond length of  $\text{Ag}-\text{S}(\text{SCN}^-)$  (0.2570 nm) is somewhat longer by 0.0049 nm than that of  $\text{Ag}-\text{S}(\text{Hpymt})$  (0.2521 nm average).  $\text{C}-\text{S}$  distances in ligand Hpymt fall within 0.1698–0.1699 nm with an average value of 0.1699 nm, consistent with the  $\text{C}=\text{S}$  bond distance and slightly shorter than that (0.1720 nm) found in  $[\text{Ag}(\text{Hpy})\text{-Cl}]_n$ , thus, it is reasonable that the ligand in the complex adopts thione configuration (**b** in Scheme 1). Four atoms Ag, S, S(1), and S(2) lie in a plane, and the  $\text{S}(1)-\text{Ag}-\text{S}$ ,  $\text{S}(2)-\text{Ag}-\text{S}$ , and  $\text{S}(2)-\text{Ag}-\text{S}(1)$  in the equatorial plane are 111.65(8), 114.96(8), 133.33(5)°, respectively. The average  $\text{Ag}-\text{Ag}$  separation is 0.3980(1) nm, preclusive of any direct metal-metal interaction.

#### Luminescent property of compound 1

The absorption spectrum of the complex measured in  $\text{CH}_3\text{OH}$  exhibits one high energy absorption band at 285 nm and one low at 352 nm, as shown in Fig. 4 (in-

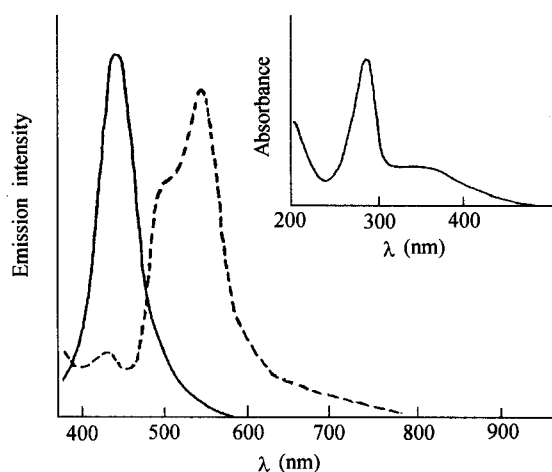


Fig. 4 UV-Vis absorption (inserted) and emission spectrum (—) of  $[\text{Ag}(\text{SC}_4\text{N}_2\text{H}_4)_2(\text{SCN})]$  in  $\text{CH}_3\text{OH}$ ; solid-state emission spectrum (---) of  $[\text{Ag}(\text{SC}_4\text{N}_2\text{H}_4)_2(\text{SCN})]_n$  at 298 K.

serted). The low-energy absorption band is assigned to the ligand to metal charge-transfer LMCT [ $(S^{2-}) \rightarrow Ag(I)$ ], which was based on the good  $\sigma$ -donating capability of sulfur atom. The luminescence spectrum of the complex was analyzed at room temperature. As shown in Fig. 4, the emissive spectrum of the complex in solid state is composed of one broad band at 568 nm and one shoulder at 502 nm ( $\lambda_{ex} = 350$  nm). However, an intense emissive band at 435 nm ( $\lambda_{ex} = 350$  nm) was observed in  $CH_3OH$ . With reference to the recent reported work on  $[Ag_4(\mu-dppm)_4(\mu_4-Se)](BF_4)_2$  compound,<sup>18</sup> the emission probably occurs from the silver-centered state of  $S \rightarrow Ag$  LMCT. It is interesting that the luminescence spectrum of the complex in solid state is different from that in solution. This may be contributed from the supramolecular secondary Ag-S interactions in solid state.

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