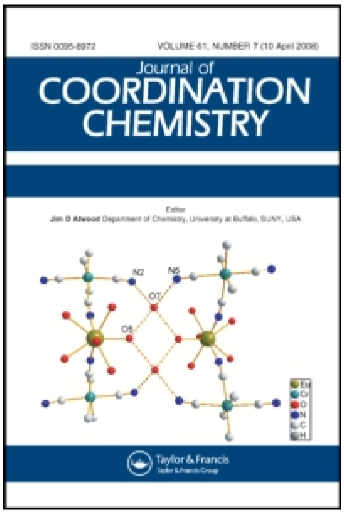

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Crystal structure of 2-aminopyridine-5-sulfonic acid and its 2D coordination polymer $[Ag(C_5H_5N_2O_3S)]_n$

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The crystal structure of an organosulfonate ligand 2-aminopyridine-5-sulfonic acid is reported here. Reaction of $AgNO_3$ and the 2-aminopyridine-5-sulfonic acid in basic ethanol/aqueous solution gave $[Ag(C_5H_5N_2O_3S)]_n$ (**1**). X-ray crystallographic study reveals that **1** is a 2D network structure constructed by strong Ag-pyridine, Ag–NH_2 interactions and weaker Ag-sulfonate interactions. The replacement of the benzene ring by the pyridine ring causes the coordination modes of the sulfonate group to change from μ^3 to μ^2. Its TG/DSC property is also discussed.

Keywords: Sulfonate complex; 2-Aminopyridine-5-sulfonic; Crystal structure

1. Introduction

Many functional polymers have been prepared with relatively "strong" coordination ligands such as N-containing ligands [1], carboxylate and phosphonate ligands [2]. "Soft" ligands such as organosulfonate has been used recently to impact meta-organic polymer properties such as flexibility due to weaker bonding to metal [3]. Studies on ligands containing "strong and soft" mixed coordinating groups give diversified structures [4]. We are interested in coordination polymers containing "strong and soft" mixed ligands such as 2-aminopyridine-5-sulfonic acid (**HL**) (scheme 1). **HL** is nearly rigid with three potential coordinating groups, –NH_2, deprotonated $-SO_3^-$ and the N of the pyridine ring. The $-SO_3^-$ is a versatile coordinating group and can coordinate to the metal in a variety of modes (scheme 2). **HL** can form not only short bridges via one sulfonate, but also long bridges via the central pyridine ring.

Reaction of $AgNO_3$ and 2-aminopyridine-5-sulfonic acid gave $[Ag(C_5H_5N_2O_3S)]_n$ (**1**), which is a 2D network incorporating both strong Ag-pyridine, Ag–NH_2 interactions and weaker Ag-sulfonate interactions. The coordination modes of the sulfonate group change from μ^3 to μ^2 when replacing the benzene by pyridine.

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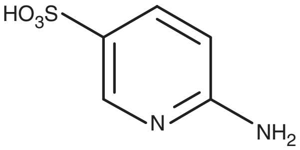
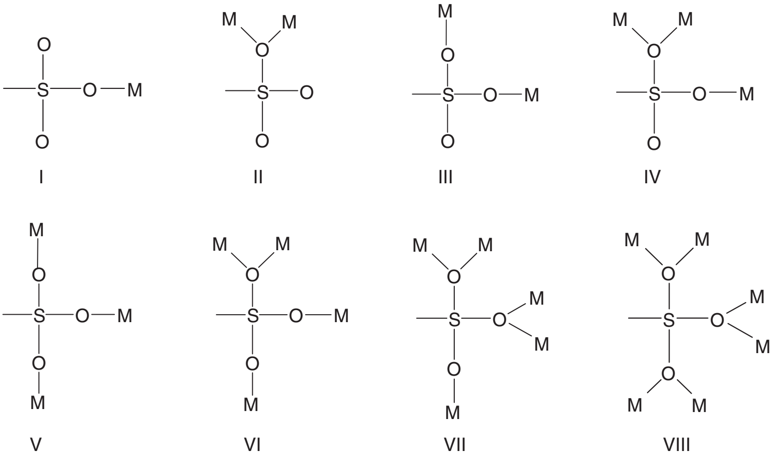


Scheme 1. Structure of 2-aminopyridine-5-sulfonic acid (**HL**).



Scheme 2. Coordination modes of sulfonate group with silver ion (M=Ag).

2. Experimental

2.1. *Main reagents and apparatus*

HL is prepared using the published method [5]. All other reagents were purchased commercially and used as received. Elemental analyses (C, H, N) were determined with a PE 2400 Elemental analyzer. Infrared spectra of KBr pellets were recorded with a BRUKER EQUINOX-55 spectrometer in the range 4000–400 cm^{-1}. Thermal analysis was performed with a NETZSCH STA 449C microanalyzer with a heating rate of $10^\circ\mathrm{C}\cdot\mathrm{min}^{-1}$ under dynamic N_2 flow rate of $30\,\mathrm{cm}^3\cdot\mathrm{min}^{-1}$.

2.2. *Synthesis of* $[Ag(C_5H_5N_2O_3S)]_n$ *(1)*

To an aqueous solution (5 mL) of silver nitrate (0.170 g, 1 mmol), 2-aminopyridine-5-sulfonic acid (0.174 g, 1 mmol) in mixed ethanol/water (15 mL 2 : 1) was added slowly. After 3 h stirring, the solution was allowed to stand at room temperature for several days, giving grey pale crystals suitable for single crystal X-ray diffraction. Elemental analysis for $AgC_5H_5N_2O_3S$. Calcd: C, 21.37; H, 1.79; N, 9.97%. Found: C, 21.28; H, 1.43; N, 9.53%. FTIR (KBr, cm^{-1}): 3435(m), 3339(m), 1644(s), 1600(s), 1562(s), 1484(s), 1392(s), 1177(s), 1131(s), 1042(s), 1008(s), and 700(m). The complex is insoluble in methanol, ethanol, acetone, *N*,*N*-dimethylformamide (DMF) and acetonitrile, but is soluble in dimethylsulfoxide (DMSO).

2.3. *X-ray crystallography*

Single crystal X-ray diffraction of the complex was performed on a BRUKER SMART 1000 CCD diffractometer equipped with a graphite monochromator situated in the incident beam for data collection. The determination of unit cell parameters and data collection were performed with Mo-Kα radiation ($\lambda = 0.71073$ Å) by ω-scan mode in the range $2.53 < \theta < 25.09°$ at 296(2) K. Semi-empirical absorption correction was applied using the SADABS program [6]. The structure was solved by direct methods [7] and refined by full-matrix least squares on F^2 using SHELXS 97 and SHELXL 97, respectively [7, 8]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions. The crystallographic data for the complex are listed in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Description of the crystal structure*

As shown in figure 1(a), silver is coordinated by N atoms from amine and pyridine, two O atoms from two different sulfonate groups of L^-. The coordination sphere of the silver is a distorted triangular pyramid with the Ag–N distance of 0.2303, 0.2322 nm and Ag–O distance of 0.2371, 0.2602 nm, similar to bond lengths in silver sulfaniliate and other silver organosulfonate complexes [9, 10]. N2A, O1A and O3A form the

Table 1. Crystal data for **1**.

Empirical formula	$C_5H_5AgN_2O_3S$
Formula weight	281.04
Temperature (K)	296(2)
Crystal system	Monoclinic
Space group	*P*2(1)/*c*
a (Å)	0.8351(5)
b (Å)	1.1489(6)
c (Å)	0.7930(4)
α (°)	90
β (°)	105.046(8)
γ (°)	90
Volume (Å^3)	0.7348(7)
Z	4
D_{Calcd} (g cm^{-3})	0.7348(7)
μ (mm^{-1})	2.988
F(000)	544
Crystal size (mm^3)	0.30 × 0.22 × 0.15
θ range for data collection (°)	2.53–25.09
Goodness-of-fit on F^2	1.034
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0682$, $wR_2 = 0.1839$
R indices (all data)	$R_1 = 0.0787$, $wR_2 = 0.1906$
Largest difference in peak and hole (e Å^{-3})	2.559 and −2.255

Table 2. Selected bond lengths (nm) and angles (°) for **1**.

Ag(1)–N(1)	0.2303(6)	Ag(1)–N(2)#1	0.2322(6)
Ag(1)–O(1)#2	0.2371(5)	S(1)–O(2)	0.1435(5)
S(1)–O(3)	0.1456(7)	S(1)–O(1)	0.1459(6)
N(2)–Ag(1)#1	0.2322(6)	O(1)–Ag(1)#2	0.2371(5)
N(1)–Ag(1)–N(2)#1	125.5(2)	N(1)–Ag(1)–O(1)#2	97.1(2)
N(2)#1–Ag(1)–O(1)#2	122.4(2)	O(2)–S(1)–O(3)	113.6(5)
O(2)–S(1)–O(1)	112.5(4)	O(3)–S(1)–O(1)	110.9(4)
O(2)–S(1)–C(4)	107.9(4)	O(3)–S(1)–C(4)	106.1(4)

Symmetry codes: #1: $-x$, $-y+1$, $-z$; #2: $-x+1$, $-y+1$, $-z+1$.

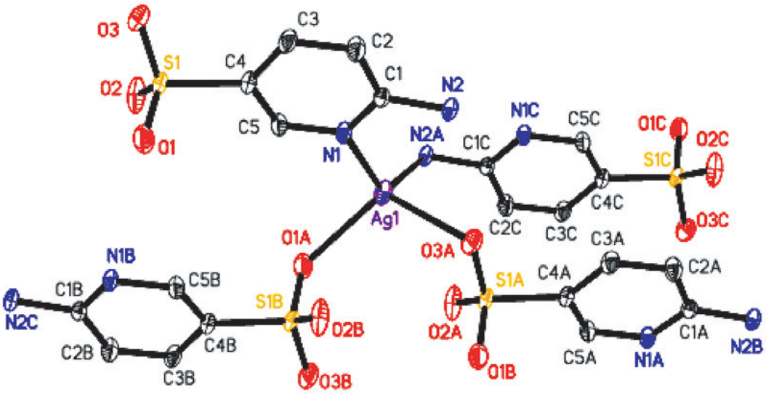


Figure 1(a). The coordination environment of Ag(I) in **1** with 30% thermal ellipsoids (H atoms are omitted for clarity).

trigonal plane and the N1 is on the top of the pyramid. The silver is nearly in the plane formed by N2A, O1A and O3A, deviating from the plane by 0.0714 nm. Each L^- links four silver ions with coordination bonds between the silver ions and the amine, the N atom of the pyridine ring, and two O atoms of the sulfonate group (figure 1b).

As expected, replacement of the phenyl ring by pyridine causes coordination of the sulfonate to change from μ^3 to μ^2, from V to III in scheme 2. This may be attributed to strong interaction between Ag and pyridine.

As illustrated in figure 2, pairs of sulfonate groups bridge pairs of silver atoms through their sulfonate oxygen atoms to give centrosymmetric dimeric units with eight-membered rings named A. Adjacent dimeric units are further linked through coordination bonds between silver atoms and the amine and the N atoms of the pyridine ring, forming another eight-membered ring named B; rings A and B alternate in the 1D silver chain. Hydrogen bonding between coordinated oxygen atoms and the amine group (with the distance N2–H2A $\cdots$ O3 = 0.2943 nm and angle N2–H2A $\cdots$ O3 = 151°) further stabilize the 1D silver chain. The pyridine ring as a bridge links the adjacent 1D silver chains resulting in a 2D inorganic-organic hybrid layer complex. Sixteen-membered rings named C are also formed between adjacent 1D silver chain. The distance between two silver atoms in rings A, B and C are 0.529, 0.3499 and 0.9375 nm, respectively, all beyond the van der Waals contact distance for Ag–Ag

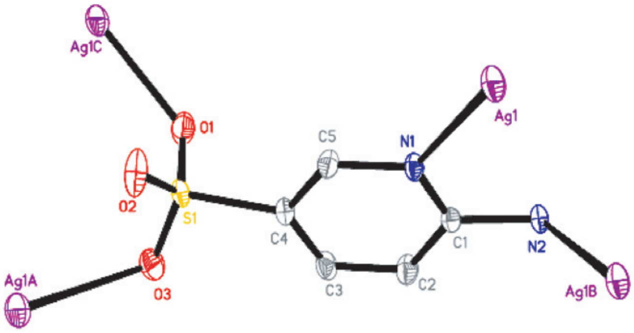


Figure 1(b). The coordination modes of L$^-$ in **1** with 30% thermal ellipsoids (H atoms are omitted for clarity).

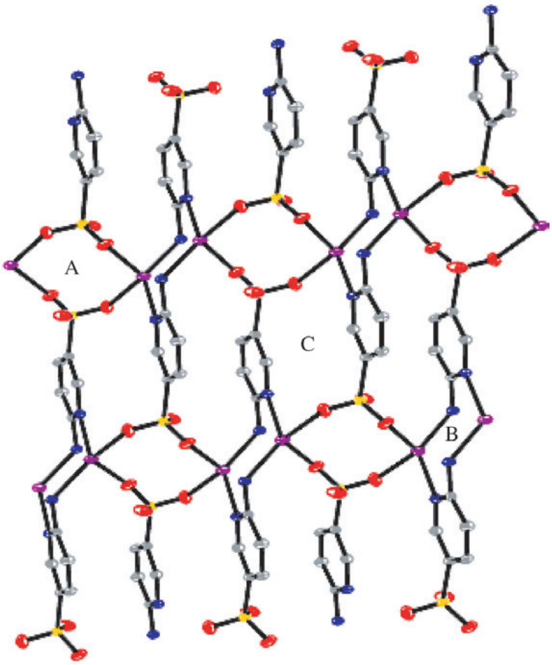


Figure 2. 2D inorganic-organic hybrid layer structure in **1**.

of 0.34 nm, so there is no Ag–Ag interaction [11]. Weak intermolecular $\pi\cdots\pi$ interactions at 0.4114 nm help to stabilize the structure [12].

3.2. *IR spectroscopy*

The IR spectra of the complex and 2-aminopyridine-5-sulfonic acid were performed as KBr pellets in the range 4000–400 cm^{-1}. 2-aminopyridine-5-sulfonic acid showed broad adsorptions at 3339 cm^{-1} and 3176 cm^{-1}, assigned as ν(N–H). The absorption at

3062 cm^{-1} corresponds to ν(C–H). The pyridine ring framework showed a strong band at 1485 cm^{-1}. Because of formation of inter-molecular coordinate bonds and hydrogen bonds, these adsorptions are shifted to 3434, 3339, 3066 and 1483 cm^{-1}, respectively, in **1**. The absorptions around 1181 cm^{-1} and 1030 cm^{-1} in 2-aminopyridine-5-sulfonic acid, attributed to $\nu_{as}(SO_3)$ and $\nu_{sym}(SO_3)$, shift to 1177 cm^{-1} and 1042 cm^{-1}, respectively, confirming involvement in coordination. The bands in the 300–600 cm^{-1} region are due to ν(Ag–N) and ν(Ag–O) vibrations in the complex. The data were reasonably in agreement with the crystallographic results.

3.3. *Thermogravimetric analysis*

Thermogravimetric analysis (TGA) has been performed at 25–800°C under N_2. The TGA curve of the complex shows that decomposition takes places in two stages in the temperature range 25–800°C. The first endothermic stage at 200–300°C shows weight loss of 28.54% and the following exothermic stage in the 550–600°C range shows weight loss of 32.91%.

4. Conclusion

The X-ray crystal structure analysis indicates that $[Ag(C_5H_5N_2O_3S)]_n$ is a 2D network constructed by both strong Ag–N interactions and weaker Ag–O (sulfonate) interaction. There exist three types of rings in the 2D network. Replacement of benzene by pyridine causes change in coordination of the sulfonate. The coordination chemistry of the **HL** with other metal ions such as alkali, alkaline ions and rare-earth metal ions, are in progress.

Supplementary data

Crystallographic data for **1** have been deposited at the Cambridge Crystallographic Data Center as supplementary publication (CCDC 609778). These data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

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References

[1] (a) O.M. Yaghi, H. Li, T.L. Groy. *Inorg. Chem.*, **36**, 4292 (1997); (b) G.J. Halder, C.J. Kepert, B. Moubaraki, K.S. Murray, J.D. Cashion. *Science*, **298**, 1762 (2002).

[2] (a) O.M. Yaghi, H. Li, T.L. Groy. *J. Am. Chem. Soc.*, **118**, 9096 (1996); (b) M. Kummo, H. Kumagai, S.M. Hughes, C.J. Kepert. *Inorg. Chem.*, **42**, 6709 (2003); (c) E. Lozano, M. Nieuwenhuyzen, S.L. James. *Chem. Eur. J.*, **7**, 2644 (2001).

[3] (a) S.A. Dalrymple, G.K.H. Shimizu. *Chem. Eur. J.*, **8**, 3010 (2002); (b) A.P. Cote, M.J. Ferguson, K.A. Khan, G.D. Enright, A.D. Kulynych, S.A. Dalrymple, G.K.H. Shimizu. *Inorg. Chem.*, **41**, 287 (2002); (c) G.K.H. Shimizu, G.D. Enright, C.I. Ratcliffe, K.F. Preston, J.L. Reid, J.A. Ripmeester. *Chem. Commun.*, 1485 (1999).

[4] (a) M.-L. Hu, Q. Miao, Q. Shi, M.-D. Ye. *Acta Cryst.*, **C60**, m460 (2004); (b) A.P. Côté, G.K.H. Shimizu. *Chem. Commun.*, 251 (2001); (c) Z.-M. Sun, J.-G. Mao, Y.-Q. Sun, H.-Y. Zeng, A. Clearfield. *Inorg. Chem.*, **43**, 336 (2004); (d) J.-S. Zhou, J.-W. Cai, L. Wang, S.-W. Ng. *Dalton Trans.*, 1493 (2004).

[5] F. Korte. *Chem. Ber.*, **85**, 1012 (1952).

[6] G.M. Sheldrick. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany (1997).

[7] G.M. Sheldrick. *SHELXS 97, Program for Crystal Structure Solution*, University of Göttingen, Germany (1997).

[8] G.M. Sheldrick. *SHELXL 97, Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).

[9] J. Schreuer, Z. Kristallogr. *New Cryst. Struct.*, **214**, 311 (1999).

[10] A.P. Côté, G.K.H. Shimizu. *Inorg. Chem.*, **43**, 6663 (2004).

[11] F.F. Li, J.F. Ma, S.Y. Song, J. Yang, Y.Y. Liu, Z.M. Su. *Inorg. Chem.*, **44**, 9374 (2005).

[12] X.M. Chen, J.W. Cai. *Single-crystal Structural Analysis: Principles and Practices*, Science Press, Beijing (2003).