

Synthesis and Structural Characterization of the 2-[(*o*-pyridyl)-sulfanylmethyl]-pyrimidine-silver(I) Complex $[\text{Ag}_2(\text{opsp})_2](\text{NO}_3)_2$

Li-Rong WEN^{1,2}, Ming LI², Gui-Long ZNAO², Xue-Mei LI²,
Ou-Yang PINGKAI¹ and Shu-Sheng ZHANG^{2*}

¹College of Science and Pharmaceutical Engineering, Nanjing University of Technology,
210009, Nanjing-CHINA

²College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology,
266042 Qingdao, Shandong-CHINA
e-mail: zhangshush@public.qd.sd.cn

Received 15.06.2004

The new silver(I) complex $[\text{Ag}_2(\text{opsp})_2](\text{NO}_3)_2$ (**1**) was synthesized by the self-assembly of AgX (X = NO_3^-) with the versatile multidentate ligand opsp (opsp = 2-[(*o*-pyridyl)-sulfanylmethyl]-pyrimidine). X-ray single-crystal diffraction analyses show that **1** is dinuclear molecule. In **1**, 1 opsp ligand acts in a bidentate mode with 2 nitrogen atoms from a pyridine ring and a pyrimidine ring coordinating to 2 Ag(I) atoms, and the Ag(I) center is 2-coordinated by 2 nitrogen atoms showing linear coordination geometry.

Key Words: Multidentate ligand; Silver(I) complex; Crystal structure; Dinuclear molecule.

Introduction

The self-assembly of metal coordination supramolecular structures is one of the most active topics current chemistry due to their potential applications as functional materials [1,2]. The ligand design is crucial in the construction of coordination polymers. In constructing ordered supramolecular assemblies, conformational rigid ligands are commonly utilized in order to reduce the unfavorable entropic factors [3–8]. The self-assembly process between labile metal ions and flexible multidentate ligands can be regarded as a result of much structural information stored in the ligands being read by metal ions through the algorithm defined by their coordination geometry. Because silver(I) exhibits high labile coordination modes with coordination number 2 to 5 all occurring, the self-assembly of coordinatively flexible Ag(I) with versatile multidentate ligands can produce various fascinating structural topologies [9–14]. In order to further investigate the interaction of versatile multidentate ligands with coordinatively flexible silver(I), we prepared a versatile multidentate ligand 2-[(*o*-pyridyl)-sulfanylmethyl]-pyrimidine, from which the silver(I) complex $[\text{Ag}_2(\text{opsp})_2](\text{NO}_3)_2$ (**1**) was obtained.

*Corresponding author

Experimental

General

The chemicals in this research work were used as purchased and without further purification. C, H and N elemental analyses were carried out using a Perkin-Elmer analyzer model 240. The IR spectra were recorded as KBr disks on a Shimadzu IR-480 infrared spectrophotometer in the 4000–600 cm^{-1} region. The ligand omsp was prepared by a similar procedure described previously [14].

Synthesis of the $[\text{Ag}_2(\text{osp})_2](\text{NO}_3)_2$

To a solution of AgNO_3 (0.068 g, 0.4 mmol) in 10 mL of acetonitrile, was added a solution of the ligand omsp (0.525 g, 0.4 mmol) in 10 mL of chloroform. The reaction mixture was stirred for 30 min, the resulting solution was filtered, and the filtrate was slowly diffused by ether to give colorless single crystals suitable for X-ray investigation. IR (cm^{-1}): 3018w, 1589s, 1560s, 1456s, 1420s, 1158w, 1146m, 1094m, 1033w, 967w, 837w, 777s, 753s, 729m. Anal. Calcd. for $\text{C}_{10}\text{H}_9\text{AgN}_4\text{O}_3\text{S}$: C 35.51, H 3.21, N 6.37; found: C 35.75, H 3.10, N 6.21.

Crystallographic Data and Structure Determination [15]

Single crystal structure measurements were made on a Bruker Smart 1000 CCD area detector with graphite monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The data were collected in the range of $2.37 < \theta < 26.50^\circ$ for **1** using the ω scan technique at a temperature of 293(2) K. LP correction was applied to the data. The structure was solved by direct methods using the SHELXL-97 [16] program and refinement on F^2 was performed using SHELXL-97 by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. All the hydrogen atoms were located in calculated positions and these were isotropically refined. Crystallographic data and experimental details for structural analyses are summarized in Table 1. The atomic coordinates and the hydrogen bonding are given in Tables 2 and 3, respectively.

Results and Discussion

Complex **1** is composed of non-coordinating NO_3^- anions and $[\text{Ag}_2(\text{osp})_2]^{2+}$ cations. The crystal structure of the dinuclear unit having a crystallographic center of symmetry is shown with atom labeling in Figure 1, and selected bond lengths and angles are listed in Table 3. Each ligand in complex **1** coordinates to 2 silver atoms in a bidentate bridging mode with its 2 nitrogen atoms to form a 14-membered binuclear metallomacrocyclic ring, and the $\text{Ag} \cdots \text{Ag}$ separation is 4.869 \AA within the ring. In complex **1** each Ag(I) atom is 2-coordinated by 2 nitrogen atoms from the pyridine ring and pyrimidine ring of different ligands with average Ag–N bond lengths of 2.216(3) \AA . The coordination geometry around the Ag(I) atom can be described as being a slightly distorted linear fashion with a N–Ag–N bond angle of 176.53(10) $^\circ$. Although the ligand omsp possesses 4 possible binding sites, that is, a sulfur atom and 3 nitrogen atoms, only 2 nitrogen atoms (a pyridine nitrogen and a pyrimidine nitrogen) engage in coordination in complex **1**.

Table 1. Crystal data and structure refinement parameters for 1.

Formula	C ₁₀ H ₉ AgN ₄ O ₃ S
Formula weight	373.14
Color/shape	colorless/block
Crystal system	Triclinic
Space group	<i>P</i> – 1
<i>a</i> / Å	8.400(2)
<i>b</i> / Å	8.670(2)
<i>c</i> / Å	9.051(3)
α /°	107.201(8)
β /°	93.313(6)
γ /°	96.331(6)
<i>V</i> / Å ³	623.0(3)
<i>Z</i>	2
<i>D</i> _(<i>calcd.</i>) /g.cm ⁻³	1.989
μ / mm ⁻¹	1.794
Crystal size/mm	0.34 × 0.22 × 0.18
Temp. /K	293(2)
θ ranges/	2.37-26.50
h/k/l	-10,9/-10,8/-11,11
Reflections collected	3571
Independent reflections	2522
Absorption correction	Empirical
No. restrains/ No. parameters	0/201
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0305 <i>wR</i> ₂ = 0.0784

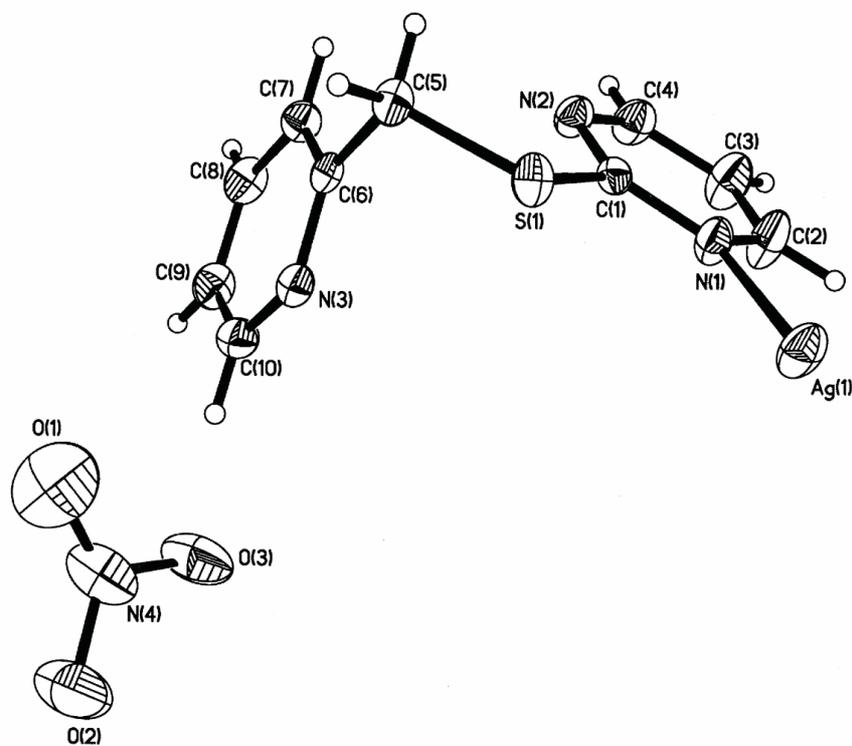

Figure 1. Perspective view of the cation of [Ag₂(opsp)₂](NO₃)₂.

Table 2. Selected bond lengths [Å] and angles [°] for complex **1**.

Ag(1)–N(1)	2.212(3)
Ag(1)–N(3) ⁱ	2.219(3)
N(1)–Ag(1)–N(3) ⁱ	176.53(10)

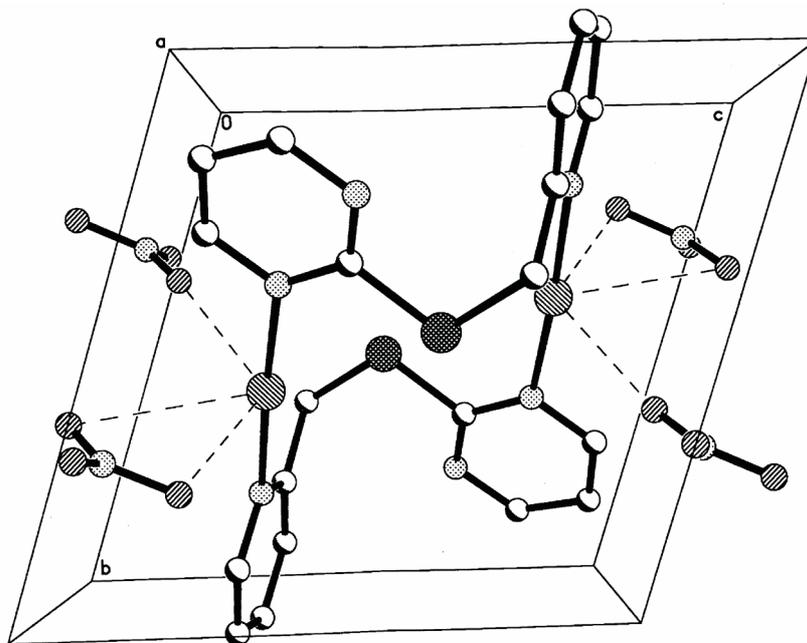
 Symmetry transformations used to generate equivalent atoms: $i -x+1, -y+1, -z+1$
Table 3. Hydrogen-bonding geometry (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A
C2–H2...O1 ⁱ	0.93	2.57	3.25	130
C3–H3...Cg2 ⁱ	0.93	2.80	3.56	140

 Symmetry codes: (i) $x, y, 1+z$.

The Ag(I) centers in a dinuclear unit show weak interactions with oxygens from the nitrate counter ions. The non-coordinating NO₃[−] anion is linked to the cation viz. C2–H2 ... O1ⁱ intramolecular interaction. Thus these dinuclear units are weakly linked by nitrate counter ions to form a double silver atom chain (Figure 2). The packing is further stabilized by C3–H3 ... Cg2 interaction [See Table 3, Cg2 denotes the centroid of the pyricine ring].

In conclusion, self-assembly between the versatile chelating ligand opsp containing nitrogen and sulfur donor atoms and coordinately flexible silver(I) salts yields the silver(I) dimer complex. Due to the counter ions, in the complex the ligand opsp and silver(I) atom show that properties of designed ligands and metal ions, as well as of counter ions, have important influences on the self-assembly process.


Figure 2. 1-D chain structure formed by weakly bridging of nitrate counter ions.

Acknowledgements

We thank the Natural Science Foundation of Shandong Province (Project Y2003B01) and the National Natural Science Foundation of China (Project 20275020) for their financial support.

References

1. M. Fujita, Y.J. Kwon, S. Washizu and K. Ogura, **J. Am. Chem. Soc.** **116**, 1151 1994.
2. Z. Tang and A.M. Guloy, **J. Am. Chem. Soc.** **121**, 452 1999.
3. M. Fujita, O. Sasaki, T. Mitsunashi, T. Fujita, J. Yazaki, K. Yamaguchi and K. Ogura, **J Chem Soc Chem Commun.**, 1535 1996.
4. B. Olenyuk, A. Fechtenkötter and P.J. Stang, **J. Chem. Soc. Dalton. Trans.** 1707 1998.
5. G.S. Hanan, C.R. Arana, J.M. Lehn and D. Fenske, **Angew. Chem. Int. Ed.** **34**, 1122 1995.
6. G.S. Hanan, C.R. Arana, J.M. Lehn, G. Baum and D. Fenske, **Chem. Eur. J.** **2**, 1292 1996.
7. P.N.W. Baxter, J.M. Lehn, J. Fischer and M.T. Youinou, **Angew. Chem. Int. Ed.** **36**, 1842 1997.
8. D.M. Bassani, J.M. Lehn, K. Fromm and D. Fenske, **Angew. Chem. Int. Ed.** **37**, 2364 1998.
9. C.M. Hartshorn and P.J. Steel, **J. Chem. Soc. Dalton. Trans.**, 3935 1998.
10. P.K. Bowyer, K.A. Porter, R.A. David, A.C. Willis and S.B. Wild, **J. Chem. Soc. Chem. Commun.**, 1153 1998.
11. S. Sailaja and M.V. Rajasekharan, **Inorg. Chem.** **39**, 4586 2000.
12. S. Liao, C.Y. Su, C.H. Yeung, A.W. Xu, H.X. Zhang and H.Q. Liu, **Inorg. Chem. Commun.** **3**, 405 2000.
13. R.H. Wang, M.C. Hong, W.P. Su, Y.C. Liang, R. Cao, Y.J. Zhao and J.B. Weng, **Inorg. Chim. Acta.** **323**, 139 2001.
14. Y.J. Zhao, M.C. Hong, Y.C. Liang, W.P. Su, R. Cao, Z.Y. Zhou and A.S. C. Chan, **Polyhedron.** **20**, 2619 2001.
15. CCDC 214321 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).
16. G.M. Sheldrick, SHELXTL V5.1 Software Reference Manual, Bruker AXS, Inc., Madison, Wisconsin, USA. 1997.