Supplementary Material (ESI) for CrystEngComm
This journal is (c) The Royal Society of Chemistry 2010

Electronic Supplementary Information

for

Anion-directed supramolecular silver(I) complexes of an O_2S_2-macrocycle: cyclic oligomer and 2-D coordination polymers

So Young Lee and Shim Sung Lee*

Department of Chemistry and Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, S. Korea. E-mail: sslee@gnu.ac.kr

Experimental Section

General: All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. ESI-mass spectra were obtained on a Thermo LCQ FLEET mass spectrometer. The FT-IR spectra were measured with a Varian 640 spectrophotometer. Thermogravimetric analyses (TGA) were performed under N_2 at a scan rate of 10 °C min^{-1} using a TA Q50 thermal analyzer. The elemental analysis was carried out on a LECO CHNS-932 elemental analyzer. The X-ray powder diffraction (XRPD) experiments were performed in a transmission mode with a Bruker GADDS diffractometer equipped with graphite monochromated Cu K_α radiation (λ = 1.54073 Å).

Preparation of $[Ag(L)NO_3]_n$ (1). $AgNO_3$ (9.4 mg, 0.055 mmol) was dissolved in methanol (2 mL) and added to a solution of **L** (20.0 mg, 0.055 mmol) in dichloromethane/methanol. The precipitate was filtered off, washed with methanol and diethyl ether and dried in vacuo. Colourless single crystals suitable for X-ray analysis were obtained by vapour diffusion with diethyl ether into DMF/DMSO solution (2 mL) (60%). Mp: 176-177 °C (decomp.). IR (KBr pellet): 2925, 2361, 2341, 1599, 1494, 1384 (NO_3^-), 1319, 1248, 1104, 1056, 756, 676 cm^{-1}. Anal. Calcd for $[C_{20}H_{26}O_6N_1Ag1S_2]$: C, 43.80; H, 4.78; S, 11.69. Found: C, 44.03; H, 4.66; S, 11.95%.

Preparation of $[Ag_4(L)_4(BF_4)_2(CH_3OH)_2](BF_4)_2$ (2). $AgBF_4$ (10.8 mg, 0.055 mmol) in dichloromethane/methanol (2 mL) was added to a solution of **L** (20.0 mg, 0.055 mmol) in dichloromethane. Slow evaporation of the solution afforded the colourless crystalline product **2** suitable for X-ray analysis (25%). Mp: 186-187 °C (decomp.). IR (KBr pellet): 2923, 2361, 2342, 1599, 1496, 1455, 1250, 1052 (BF_4^-), 767, 675 cm^{-1}. Anal. Calcd for $[C_{82}H_{106}Ag_4B_4F_{16}O_{11}S_8]$: C, 42.77; H, 4.64; S, 11.14. Found: C, 42.35; H, 4.46; S, 11.51%. Mass spectrum *m/z* (ESI-MS) 467.3 $[Ag(\mathbf{L})]^+$, 826.8 $[Ag(\mathbf{L})_2]^+$, 1022.7 $[Ag_2(\mathbf{L})_2(BF_4)]^+$, 1579.3 $[Ag_3(\mathbf{L})_3(BF_4)_2]^+$ and 1772.7 $[Ag_4(\mathbf{L})_3(BF_4)_3]^+$.

Preparation of $[Ag(L)CF_3SO_3]_n$ (3). $AgCF_3SO_3$ (14.3 mg, 0.055 mmol) in methanol (2 mL) was added to a solution of **L** (20.0 mg, 0.055 mmol) in dichloromethane. Slow evaporation of the solution afforded the colourless crystalline product **3** suitable for X-ray analysis (30%). Mp: 184-185 °C (decomp.). IR (KBr pellet) 2948, 1599, 1499, 1452, 1425, 1282, 1241, 1221, 1160, 1109, 1024, 990, 764, 636, 515 cm^{-1}. Anal. Calcd for $[C_{21}H_{24}Ag_2F_3O_5S_3]$: C, 40.85; H, 3.92; S, 15.58. Found: C, 41.35; H, 3.771; S, 15.95%.

Preparation of $[Ag(L)CF_3CO_2]_n$ (4). $AgCF_3CO_2$ (12.3 mg, 0.055 mmol) in methanol (2 mL) was added to a solution of **L** (20.0 mg, 0.055 mmol) in dichloromethane. Slow evaporation of the solution afforded the colourless crystalline product **4** suitable for X-ray analysis (25%). Mp: 176-177 °C (decomp.). IR (KBr pellet) 2935, 2878, 1636, 1599, 1496, 1454, 1298, 1248, 1193, 1129, 1108, 997, 796, 751, 720 cm^{-1}. Anal. Calcd for $[C_{22}H_{24}Ag_1F_3O_4S_2]$: C, 45.45; H, 4.16. Found: C, 45.72; H, 4.16%.

X-ray Crystallographic Analysis

Crystal data for **1** and **3**: The diffraction data were measured at 173 K on a Bruker SMART CCD diffractometer equipped with graphite monochromated Mo K_α radiation (λ = 0.71073 Å). The cell parameters for the compounds were obtained from a least-squares refinement of the spot (from 45 collected frames) using the SMART program. The intensity data were processed using the Saint Plus program. All of the calculations for the structure determination were carried out using the SHELXTL package (version 6.22).[S1] Absorption corrections were applied by using XPREP and SADABS.[S2]

Crystal data for **2**: The diffraction data were collected on a Bruker SMART APEX II ULTRA diffractometer equipped with graphite monochromated Mo K_α radiation (λ = 0.71073 Å) generated by a rotating anode. The cell parameters for the compounds were obtained from a least-squares refinement of the spot (from 36 collected frames). Data collection, data reduction, and semi-empirical absorption correction were carried out using the software package of APEX2.[S3] All of the calculations for the structure determination were carried out using the SHELXTL package.[S1]

Crystal data for **4**: The diffraction data were measured at 100 K with synchrotron radiation [λ 0.77000 Å] on a 4AMXW ADSC Quantum-210 detector with a platinum coated double crystal monochromator at the Pohang Accelerator Laboratory, Korea. The HKL2000 (*V.* 0.98.694)[S3] software package was used for data collection, cell refinement, reduction, and absorption correction. Collected data were corrected for absorbance using SADABS based upon Laue symmetry using equivalent reflections.

References

S1. G. M. Sheldrick, Bruker, *SHELXTL-PC Version 6.22 Program for Solution and Refinement of Crystal Structures*; Bruker AXS Inc., Madison, Wisconsin, U.S.A. 2001.

S2. G. M. Sheldrick, SADABS Software for Empirical Absorption Correction; University of Göttingen: Göttingen, Germany, 2000.

S3. Bruker, *APEX2 Version 2009.1-0 Data collection and Processing Software*; Bruker AXS Inc., Madison, Wisconsin, U.S.A., 2008.

S3. Z. Otwinowski, W. Minor, in *Methods in Enzymology*, ed. C. W. Carter, Jr., R. M. Sweet, Academic Press, New York, 1997, vol. 276, part A, pp. 307-326.

Table S1 Crystal data and structural refinement for **1-4**

	1	**2**	**3**	**4**
Formula	$C_{20}H_{24}AgNO_5S_2$	$C_{82}H_{102}Ag_4B_4F_{16}O_{10}S_8$	$C_{21}H_{24}AgF_3O_5S_3$	$C_{44}H_{48}Ag_2F_6O_8S_4$
Formula weight	530.39	2282.84	617.45	1162.80
Temperature	173(2)	173(2)	173(2)	100(2)
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	$Pca2_1$	P-1	$P2_1/c$	$P2_1/n$
Z	4	1	4	4
a (Å)	25.0250(15)	12.851(2)	10.7047(7)	14.918(3)
b (Å)	5.5727(3)	13.297(2)	17.0508(11)	15.796(3)
c (Å)	14.7787(9)	14.903(2)	13.6200(9)	18.970(4)
α (°)	90	112.100(7)	90.00	90.00
β (°)	90	107.570(6)	105.185(2)	96.16(3)
γ (°)	90	91.354(7)	90.00	90.00
V (Å^3)	2061.0(2)	2222.0(6)	2399.2(3)	4444.4(15)
D_{calc} (g/cm^3)	1.709	1.706	1.709	1.738
$2\theta_{max}$ (°)	53.98	52.00	56.58	52.60
R	0.0441	0.0506	0.0424	0.0592
wR	0.1009	0.1178	0.0805	0.1732
No. of reflection used [>2σ(I)]	4353 [R(int) = 0.0873]	8729 [R(int) = 0.0406]	5915 [R(int) = 0.0335]	7018 [R(int) = 0.0724]
Diffractometer	Bruker SMART CCD	Bruker SMART APEX II ULTRA	Bruker SMART CCD	4AMXW ADSC Quantum-210
Structure determination	SHELXTL	SHELXTL	SHELXTL	SHELXTL
Refinement	full-matrix	full-matrix	full-matrix	full-matrix

Table S2 Selected bond lengths (Å) and bond angles (°) for **1**

S1A-Ag1	2.509(1)	Ag1-S2	2.513(2)
Ag1-O3	2.612(3)	Ag1-O4	2.645(4)
S1A-Ag1-S2	148.1(1)	S2-Ag1-O4	109.3(1)
S2-Ag1-O3	97.0(2)	O3-Ag1-S1A	95.7(1)

Symmetry operation (A) -*x* + 3/2, *y*, *z* - 1/2

Table S3 Selected bond lengths (Å) and bond angles (°) for **2**

Ag1-S1	2.525(1)	Ag1-S2	2.539(1)
Ag1-O1	2.668 (5)	Ag2-S4	2.468(2)
Ag2-S2	2.459(1)	Ag2-O5	2.423(4)
S1-Ag1-S2	99.2(2)	S1-Ag1-O1	79.4 (1)
O1-Ag1-S2	98.2 (1)	O5-Ag2-S4	107.8(1)
O5-Ag2-S2	103.8(1)	S2-Ag2-S4	134.9(2)

Table S4 Selected bond lengths (Å) and bond angles (°) for **3**

Ag1-S1	2.441(1)	Ag1-O4	2.448(4)
Ag1-S2A	2.459(1)	Ag1-O5B	2.586(5)
S1-Ag1-O4	115.7(1)	S1-Ag1-S2A	141.5(1)
S2A-Ag1-O5B	91.8(1)	O4-Ag1-O5B	97.1(2)

Symmetry operation (A) *x*, -*y* + 1/2, *z* - 1/2, (B) -*x* + 1,-*y* + 1,-*z* - 1

Table S5 Selected bond lengths (Å) and bond angles (°) for **4**

Ag1-O6	2.374(4)	Ag1-S2	2.517(2)
Ag1-O8	2.589(5)	Ag2-O8	2.456(5)
Ag1-S3A	2.465(2)	Ag2-S4	2.540(2)
Ag2-O6	2.552(4)	Ag2-S1B	2.495(2)
O6-Ag1-S3A	126.1(1)	S3A-Ag1-S2	127.4(1)
O6-Ag1-O8	80.0(2)	S2-Ag1-O8	93.5(1)
O8-Ag2-S1B	133.6(1)	S1B-Ag2-S4	131.3(1)
O8-Ag2-O6	79.2(1)	S4-Ag2-O6	101.5(1)

Symmetry operation (A) -*x* + 3/2, *y* + 1/2,-*z* + 1/2, (B) -*x* + 1/2, *y* - 1/2,-*z* + 1/2