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Guest-dependent three nitrate–water aggregations encapsulated in silver(I)-bipyridine supramolecular frameworks

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Content

(1) Experiment details

Materials and General Methods.

All the reagents and solvents employed were commercially available and used as received without further purification. Infrared spectra were recorded on a Nicolet AVATAT FT-IR330 spectrometer as KBr pellets in the frequency range 4000-400 cm^{-1}. The elemental analyses (C, H, N contents) were determined on a CE instruments EA 1110 analyzer. Photoluminescence measurements were performed on a Hitachi F-7000 fluorescence spectrophotometer with solid powder on a 1 cm quartz round plate. Thermogravimetric (TG) curves were measured from 30 to 750 ^{o}C on a NETZSCH TG 209 F1 Iris® Thermogravimetric Analyser at the heating rate 10 ^{o}C/min under N_2 atmosphere (20 mL/min).

(2) Synthesis of 1 - 3

Synthesis of $[Ag_4(bipy)_4 \cdot o\text{-}abn \cdot 4NO_3 \cdot 6H_2O]_n$ (1)

Reaction of a mixture of $AgNO_3$ (17 mg, 0.1 mmol), bipy·$2H_2O$ (19.4 mg, 0.1 mmol) and *o*-abn (12 mg, 0.1 mmol) in methanol-H_2O (6 mL, v:v = 1:2) under the ultrasonic condition (160W, 40 KHz, 40 min, room temperature). Then aqueous NH_3 solution (25%, 0.5 mL) was dropped into the mixture to give a clear solution. The resultant solution was allowed to evaporate slowly in darkness at room temperature for several days to give pale-yellow crystals of **1** (Yield: 51%, based on silver). Anal. Calc. (found) for $C_{47}H_{50}Ag_4N_{14}O_{18}$: C, 36.88 (36.69); H, 3.29 (3.58); N, 12.81 (12.30) %. IR (KBr): ν(cm^{-1}) = 3412 (s), 2201 (m), 1652 (m), 1600 (s), 1486 (m), 1382 (s), 1225 (m), 807 (m).

Synthesis of $[Ag_3(bipy)_3 \cdot m\text{-}abn \cdot 3NO_3 \cdot 2H_2O]_n$ (2):

Synthesis of **2** is the similar to that of **1**, but using *m*-abn (12 mg, 0.1 mmol) instead of *o*-abn. The crystals were isolated by filtration and dried in air. (Yield: 71%, based on silver). Anal. Calc. (found) for $C_{37}H_{34}Ag_3N_{11}O_{11}$: C, 39.25 (40.09); H, 3.03 (2.88); N, 13.61 (13.30) %. IR (KBr): ν(cm^{-1}) = 3446 (s), 2226 (m), 1599 (s), 1390 (s), 1216 (m), 815 (w).

Synthesis of $[Ag_2(bipy)_2 \cdot p\text{-}abn \cdot 2NO_3 \cdot H_2O]_n$ (3)

Synthesis of **3** is the similar to that of **1**, but using *p*-abn (12 mg, 0.1 mmol) instead of *o*-abn. The crystals were isolated by filtration and dried in air. (Yield: 65 %, based on silver). Anal. Calc. (found) for $C_{27}H_{24}Ag_2N_8O_7$: C, 41.14 (41.00); H, 3.07 (3.28); N, 14.22 (14.54) %. IR (KBr): ν(cm^{-1}) = 3441 (s), 2205 (s), 1599 (s), 1384 (s), 1225 (m), 1161 (w), 1069 (w), 801 (w).

(3) X-ray Crystallography

Single crystals of the complexes **1**-**3** with appropriate dimensions were chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collection. Data were collected on a Rigaku R–AXIS RAPID Image Plate single–crystal diffractometer (Mo Kα radiation, λ= 0.71073 Å) equipped with an Oxford Cryostream low-temperature apparatus operating at 50 kV and 90 mA in ω scan mode for **1**-**3**. A total of 44 × 5.00° oscillation images was collected, each being exposed for 5.0 min. Absorption correction was applied by correction of symmetry–equivalent reflections using the ABSCOR program.[1] In all cases, the highest possible space group was chosen. All structures were solved by direct methods using SHELXS–97[2] and refined on F^2 by full-matrix least-squares procedures with SHELXL–97.[3] Atoms were located from iterative examination of difference *F*-maps following least squares refinements of the earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2 – 1.5 times U_{eq} of the attached C atoms. The hydrogen atoms attached to oxygen were refined with O–H = 0.85 Å, and U_{iso}(H) = 1.2U_{eq}(O). All structures were examined using the Addsym subroutine of PLATON[4] to assure that no additional symmetry could be applied to the models. In **1**, The highest peaks 1.29 and the deepest hole -1.10 locate close to Ag with distances of 0.98 and 1.38 Å, respectively. In **3**, The highest peaks 1.42 and the deepest hole -0.90 locate close to Ag with distances of 0.88 and 0.76 Å, respectively. These could be ascribed to the ghosts of the heavy atom (Fourier truncation errors).

(1) Higashi, T. *ABSCOR, Empirical Absorption Correction based on Fourier Series Approximation*, Rigaku Corporation, Tokyo, 1995.

(2) Sheldrick, G. M. *SHELXS-97, Program for X-ray Crystal Structure Determination*, University of Gottingen, Germany, 1997.

(3) Sheldrick, G. M. *SHELXL-97, Program for X-ray Crystal Structure Refinement*, University of Gottingen, Germany, 1997.

(4) Spek,A. L. *Implemented as the PLATON Procedure, a Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 1998.

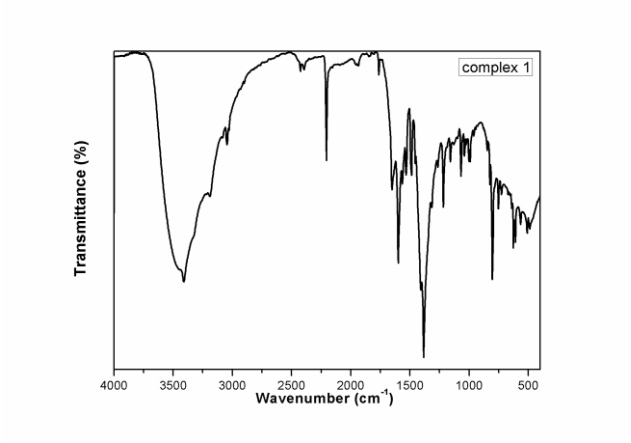
(4) Table S1: Crystal data for 1-3

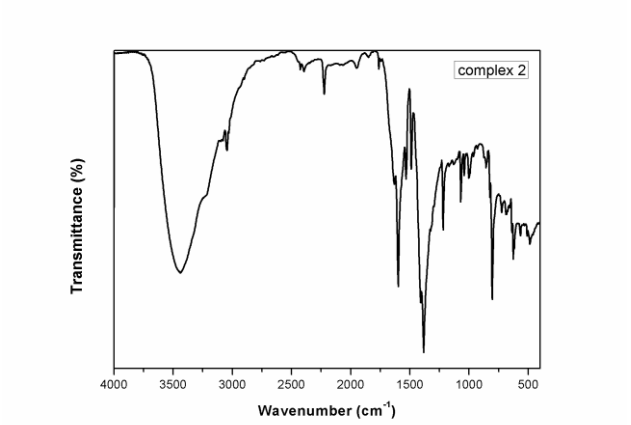
Empirical formula	$C_{47}H_{50}Ag_4N_{14}O_{18}$ (**1**)	$C_{37}H_{34}Ag_3N_{11}O_{11}$ (**2**)	$C_{27}H_{24}Ag_2N_8O_7$ (**3**)
Formula weight	1530.49	1132.36	788.28
Temperature/K	173(2)	293(2)	173(2)
Crystal system	triclinic	monoclinic	monoclinic
Space group	*P*-1	*Cc*	$P2_1/c$
a/Å	11.328(2)	19.314(4)	14.010(4)
b/Å	13.975(3)	12.146(2)	11.380(3)
c/Å	18.270(3)	17.814(4)	18.085(5)
α/°	106.019(4)	90.00	90.00
β/°	100.171(4)	106.86(3)	101.627(5)
γ/°	102.572(3)	90.00	90.00
Volume/$Å^3$	2625.6(9)	3999.4(14)	2824.2(13)
Z	2	4	4
$\rho_{calc}mg/mm^3$	1.936	1.881	1.854
μ/mm^{-1}	1.559	1.530	1.449
F(000)	1524.0	2248.0	1568.0
Crystal size/mm^3	0.40 × 0.40 × 0.20	0.10 × 0.10 × 0.08	0.40 × 0.40 × 0.20
2Θ range for data collection	2.4 to 50°	6.7 to 49.98°	2.96 to 50°
Index ranges	$-13 \le h \le 13$, $-16 \le k \le 13$, $-17 \le l \le 21$	$-20 \le h \le 22$, $-14 \le k \le 14$, $-21 \le l \le 21$	$-16 \le h \le 15$, $-13 \le k \le 8$, $-21 \le l \le 20$
Reflections collected	13452	15101	13681
Independent reflections	9130[R(int) = 0.0315]	6519[R(int) = 0.0381]	4950[R(int) = 0.0606]
Data/restraints/parameters	9130/6/757	6519/2/559	4950/30/397
Goodness-of-fit on F^2	1.169	1.013	1.189
Final R indexes [I>=2σ (I)]	R_1 = 0.0661, wR_2 = 0.1228	R_1 = 0.0306, wR_2 = 0.0657	R_1 = 0.0767, wR_2 = 0.1979
Final R indexes [all data]	R_1 = 0.0828, wR_2 = 0.1308	R_1 = 0.0344, wR_2 = 0.0688	R_1 = 0.0994, wR_2 = 0.2106
Largest diff. peak/hole / e $Å^{-3}$	1.29/-1.10	0.37/-0.55	1.60/-1.00
Flack parameter	N/A	0.01(2)	N/A

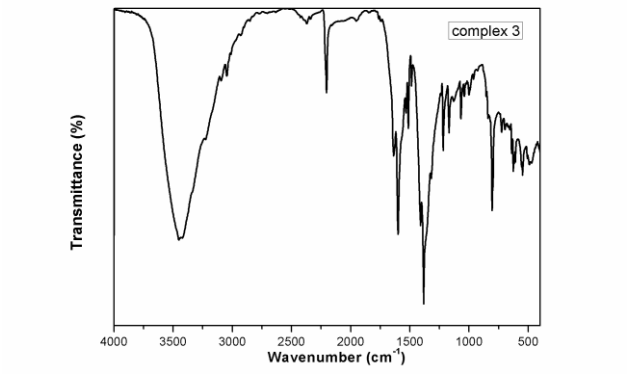
(5) Table S2 The C-H···π interactions in 1-3

Compound **1**			
C-H···Cg	H···Cg(Å)	C···Cg(Å)	H···Cg(Å)
C7-H7···Cg1	2.79	3.630(8)	148
C37-H37···Cg1	2.65	3.516(7)	151
Cg1: C41/C42/C43/C44/C45/C46			
Compound **2**			
C2-H2···Cg1A	2.96	3.846(6)	160
C14-H14···Cg1B	2.86	3.735(6)	158
Cg1: C31/C32/C33/C34/C35/C36. Symmetry code: (A) x, 1-y, 1/2+z. (B) -1/2+x, 3/2-y, -1/2+z			
Compound **3**			
C4-H4···Cg1C	2.63	3.460(10)	146
Cg1: C22/C23/C24/C25/C26/C27. Symmetry code: (C) 1-x, 1-y, 1-z.			

(6) Fig. S1: IR of 1-3







(7) Fig. S2: The powder XRD patterns and the simulated one from the single-crystal diffraction data for complexes 1-3