Supporting Information for

Nanoporous Ag(I)-MOF showing unique selective adsorption of benzene among its organic analogues

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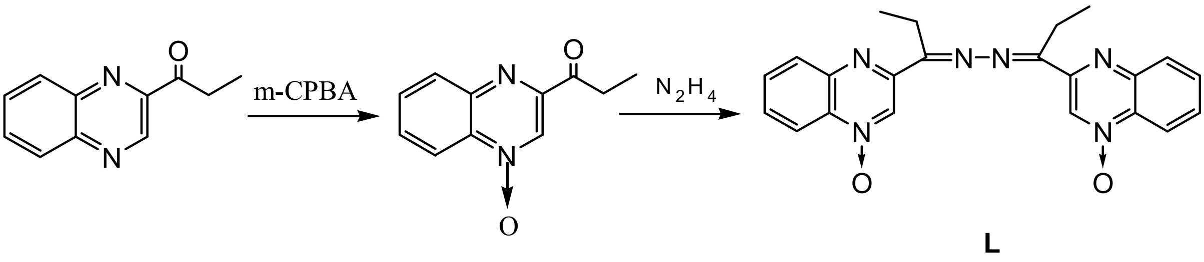
Experimental section

Materials and Methods. $AgSbF_6$ (Acros) was used as obtained without further purification. Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 400-4000 cm^{-1} range using a Perkin-Elmer 1600 FT-IR spectrometer. Elemental analyses were performed on a Perkin-Elmer model 2400 analyzer. ^1H NMR data were collected using an AM-300 spectrometer. Chemical shifts are reported in δ relative to TMS. All fluorescence measurements were carried out on a Cary Eclipse spectrofluorometer (Varian, Australia) equipped with a xenon lamp and quartz carrier at room temperature. Thermogravimetric analyses were carried out using a TA Instrument SDT 2960 simultaneous DTA-TGA under flowing nitrogen at a heating rate of 10°C/min. Electrical conductivity was performed on Agilent Technologies (4294A-ATO-20150). XRD pattern were obtained on a D8 ADVANCE X-ray powder diffraction (XRD) with Cu Kα radiation (λ = 1.5405 Å).

Synthesis of 2-propionyl-quinoxaline-*N*-oxide.



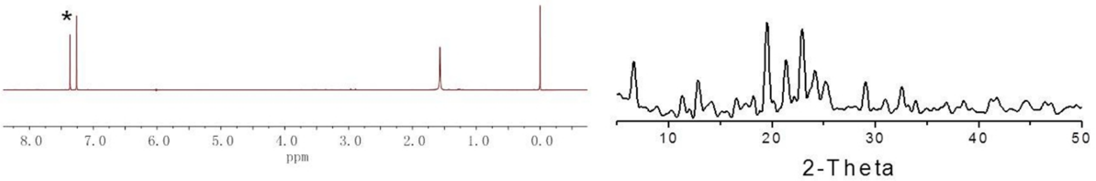
Scheme 1. Synthesis of **L**.

A mixture of 1-(quinoxalin-3-yl)propan-1-one (2.5g, 13.5mmol) and m-CPBA (4.6g, 26.5mmol) in THF (50mL) was refluxed for 48 h. A saturated aqueous Na_2CO_3 solution (25 - 30mL) was added until the resulting mixture became basic. The aqueous layer was extracted with 2 × 50mL CH_2Cl_2 and the combined organic layers were dried over Na_2SO_4. The crude product obtained under vacuum was further purified on a silica gel column using CH_2Cl_2 as the eluent to afford 2-propionyl-quinoxaline-*N*-oxide as a light yellow crystalline solid (1.6g, yield: 59%). m.p. = 126.6-127.2°C. ^1H NMR (300MHz, DMSO, 25°C, TMS): δ = 8.79(s, 1H, -C_4HN_2O), 8.47(d, 1H, -C_6H_4), 8.25(d, 1H, -C_6H_4), 8.00(m, 2H, -C_6H_4), 3.27(q, 2H, -CH_2-), 1.14(t, 3H, -CH_3). IR (KBr pellet cm^{-1}): 3416.17(s), 1700.70(m), 1638.02(m), 1618.68(m), 1576.79(w), 1525.22(w), 1496.87(w), 1457.83(w), 1399.57(s), 1337.68(w), 1248.17(w), 1183.17(w), 1140.05(w), 1084.03(w), 1027.12(w), 902.34(w), 866.29(w), 784.42(w), 605.59(w).

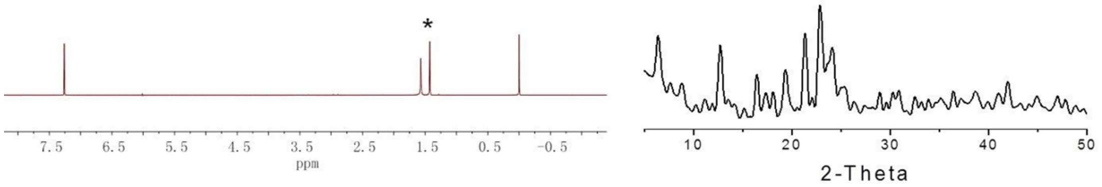
Synthesis of L. 2-propionyl-quinoxaline-*N*-oxide (1.7g, 10mmol) was dissolved in ethanol (50mL), followed by dropwise addition of the hydrazine solution (80wt.% solution in water, 0.3g, 5mmol). After two drops of formic acid were added, the mixture was refluxed for 48 h. After the solvent was removed under vacuum, the residue was extracted with methylene chloride and washed with water several times. The organic phase was dried over $MgSO_4$, filtered, and, upon removal of the solvent, an analytically pure yellow crystalline solid was obtained in 85% yield. m.p. = 190.4-191.8°C. ^1H NMR (300MHz, DMSO, 25°C, TMS): δ = 9.09(s, 2H, -C_4HN_2O), 8.52(d, 2H, -C_6H_4), 8.26(d, 2H, -C_6H_4), 8.00(m, 4H, -C_6H_4), 3.06(q, 4H, 2-CH_2-), 1.16(t, 6H, 2-CH_3). IR (KBr pellet cm^{-1}): 3420.27(s), 1638.72(m), 1574.1(m), 1523.55(w), 1489.92(w), 1456.57(w), 1414.08(w), 1373.46(s), 1248.24(w), 1216.04(w), 1136.37(w), 1088.78(w), 909.51(m), 857.16(w), 773.2 (s), 606.53(w). Elemental analysis (%) Calcd for $C_{22}H_{20}N_6O_2$: C 65.99, H 5.03, N 20.99. Found: C 66.36, H 5.0, N 16.50.

Benzene and its analogues adsorption.

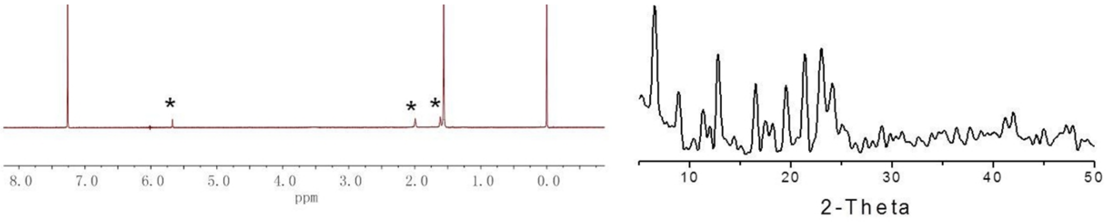
Liquid phase. 1' was respectively immersed in benzene, cyclohexane, cyclohexene, *o*-, *m*-, *p*-xylene liquid for a week at room temperature, all of these guest molecules can be incorporated into the framework of **1'** to generate benzene$\subset$**1'** (**1'a**), cyclohexane$\subset$**1'** (**1'b**), cyclohexene$\subset$**1'** (**1'c**), *o*-xylene$\subset$**1'** (**1'd**), *m*-xylene$\subset$**1'** (**1'e**), *p*-xylene$\subset$**1'** (**1'f**).



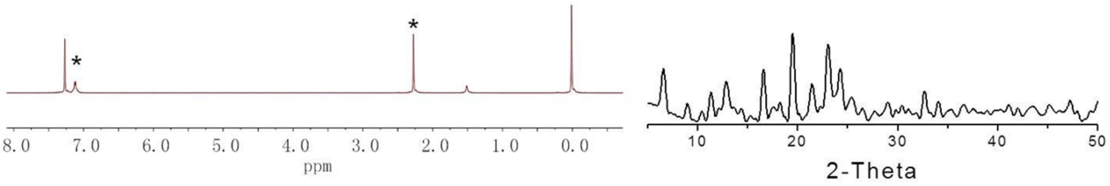
1’a, benzene$\subset$$Ag_3L_2$



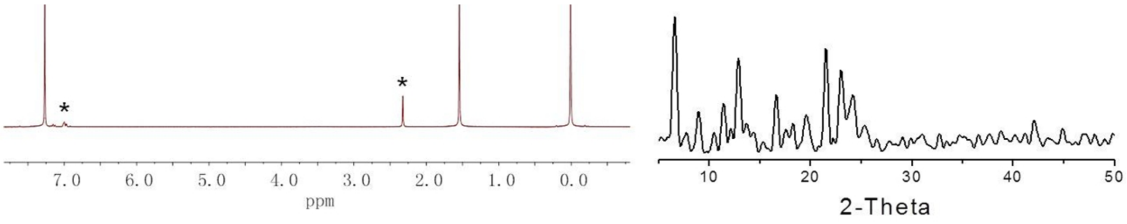
1’b, cyclohexane$\subset$$Ag_3L_2$



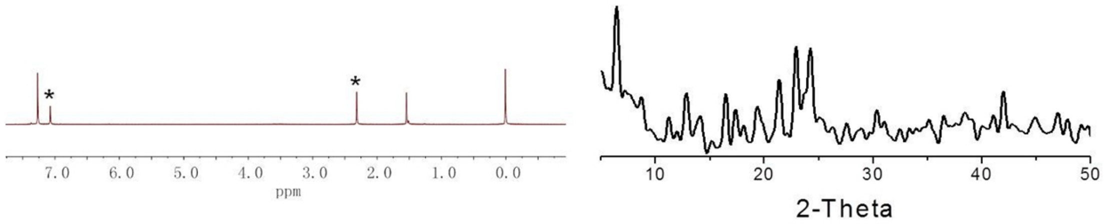
1’c, cyclohexene$\subset$$Ag_3L_2$



1’d, *o*-xylene$\subset$$Ag_3L_2$



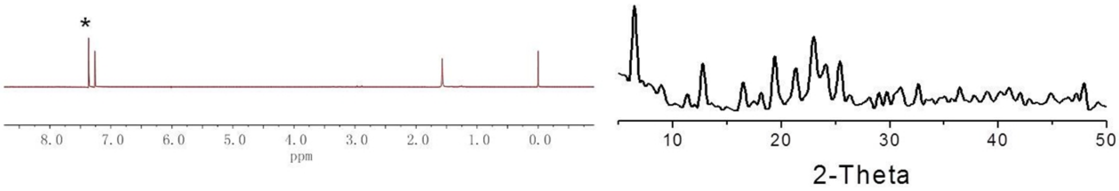
1’e, *m*-xylene$\subset$$Ag_3L_2$



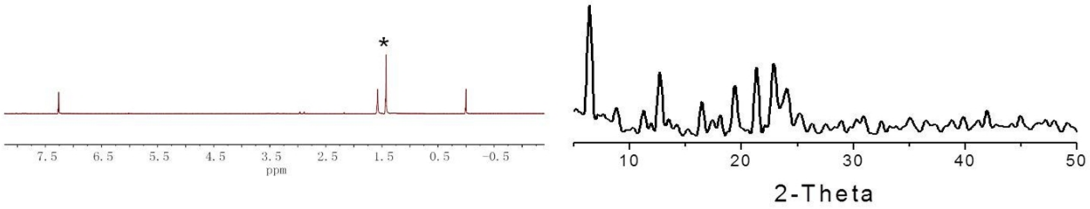
1’f, *p*-xylene$\subset$Ag$_3$L$_2$

Fig. S1 ^{1}H NMR spectra (CDCl$_3$ extraction) and XRPD patterns of **1’a-1’f**. In liquid phase, both benzene and its organic analogues can be uploaded in **1’**, and the framework of **1** is intact during the adsorption process.

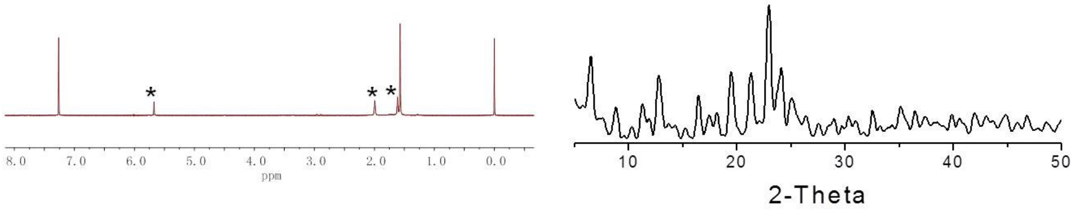
Vapor phase. 1’ was respectively exposed to benzene, cyclohexane, cyclohexene, and *o*-, *m*-, *p*-xylene vapors for a week at room temperature, all of these guest molecules can be incorporated into the framework of **1’** to generate benzene$\subset$**1’** (**1’a’**), cyclohexane$\subset$**1’** (**1’b’**), cyclohexene$\subset$**1’** (**1’c’**), *o*-xylene$\subset$**1’** (**1’d’**), *m*-xylene$\subset$**1’** (**1’e’**), *p*-xylene$\subset$**1’** (**1’f’**).



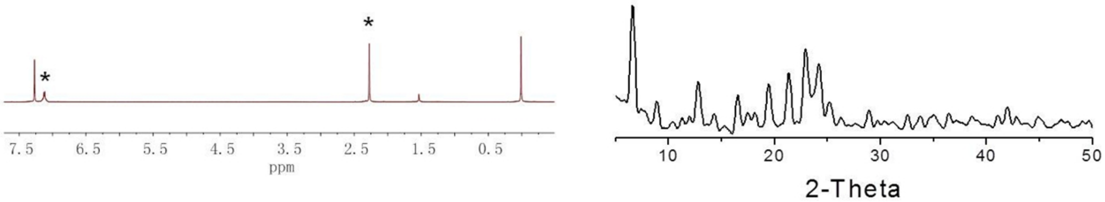
1’a’, benzene$\subset$Ag$_3$L$_2$



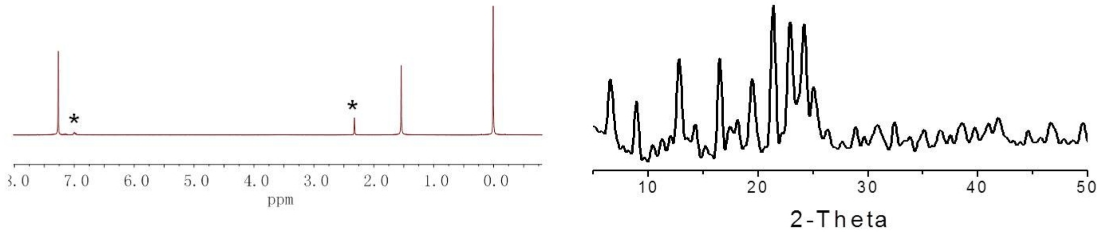
1’b’, cyclohexane$\subset$Ag$_3$L$_2$



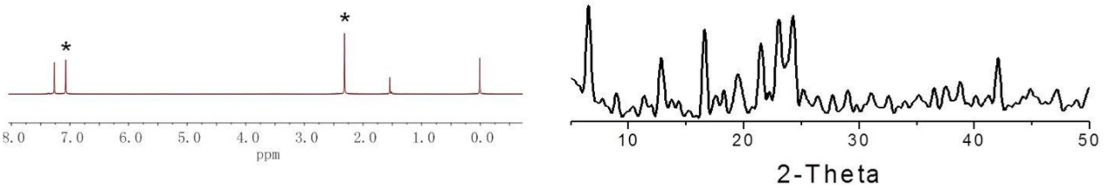
1’c’, cyclohexene$\subset$Ag$_3$L$_2$



1’d’, *o*-xylene$\subset\mathrm{Ag_3L_2}$



1’e’, *m*-xylene$\subset\mathrm{Ag_3L_2}$



1’f’, *p*-xylene$\subset\mathrm{Ag_3L_2}$

Fig. S2 ^{1}H NMR spectra ($CDCl_3$ extraction) and XRPD patterns of **1’a-1’f**. In vapor phase, both benzene and its organic homologues can be uploaded in **1’**, and the framework of **1** is intact during the adsorption process.

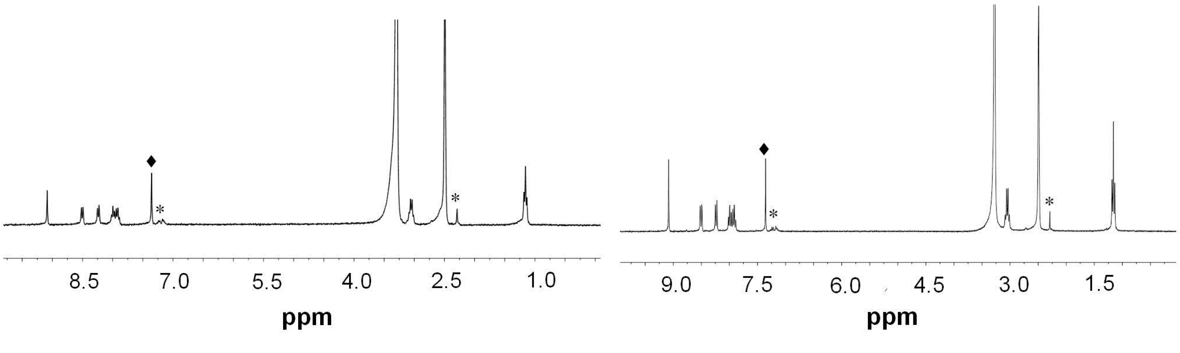


Fig. S3. ^{1}H NMR spectra (DMSO-d^6) of the samples obtained by immersing of **1’** in a mixed-solvent (left) and exposed to a mixed-vapor system (right) that consists of equimolar benzene and toluene. As shown in the figure, the $\mathrm{Ag_3L_2}$ framework cannot effectively separate benzene and toluene. The benzene and toluene are marked as “◆” and “∗”, respectively.

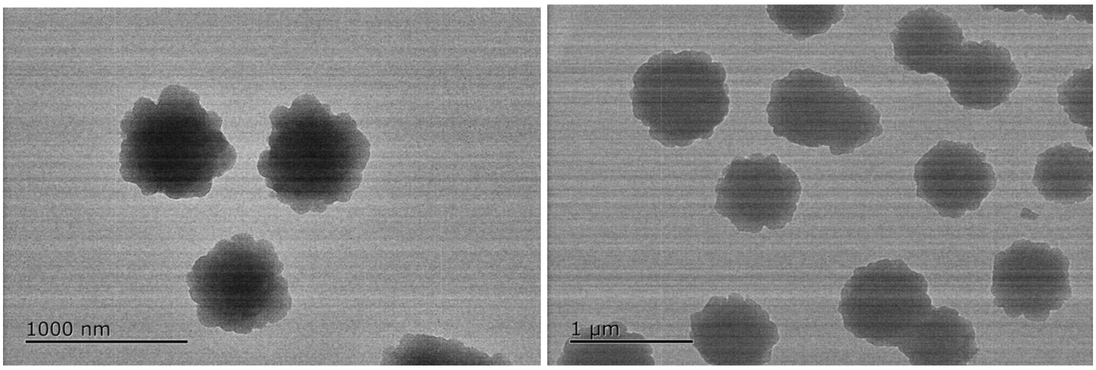


Fig. S4 TEM images of **1**.

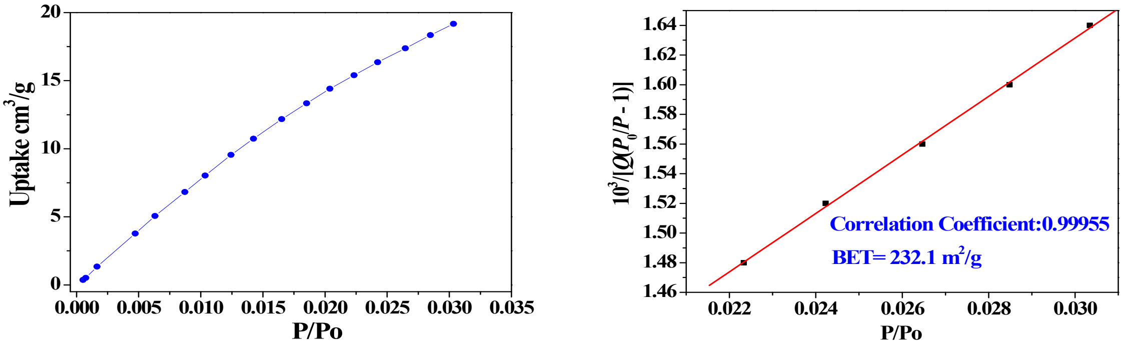


Fig. S5 BET measurement using CO_2 at 273 K (Left: CO_2 isotherm of Ag(I)-MOF collected at 273 K. Right: The BET plot for Ag(I)-MOF in the chosen range ($P/P_0 = 0.02 – 0.03$).[1]

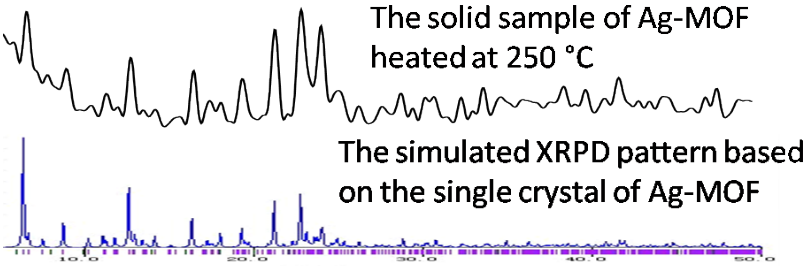


Fig. S6 The framework of **1** is thermally stable up to 250°C, which was confirmed by the XRPD data collected after the sample heated at 250°C.

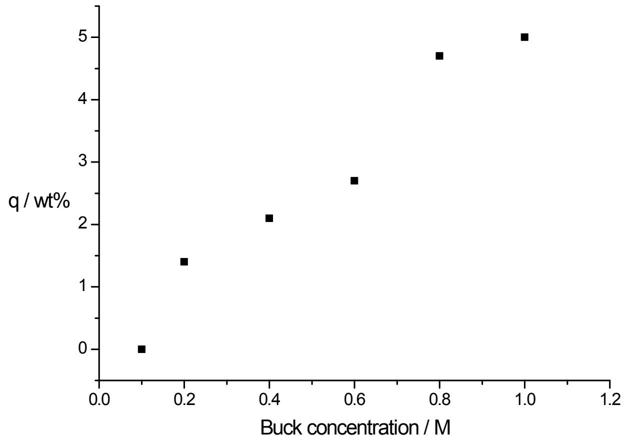


Fig. S7. Benzene adsorption on Ag(I)-MOF in hexane at 298 K: uptake q of benzene from hexane as a function of the adsorbate concentration.[2] Batch adsorption procedure: Sample of **1'** (10 mg) was added to six GC vials, to which hexane solutions of benzene with different concentrations (0.1, 0.2, 0.4, 0.6, 0.8, 1.0M, respectively) were sequentially added. After one week, the benzene loaded samples were obtained for the adsorption isotherm.

Table S1. Interatomic Distances (Å) and Bond Angles (deg) for **1.**

Ag(1)-N(2)	2.253(9)	Ag(1)-N(3)	2.395(8)
Ag(2)-N(5)	2.216(12)	Ag(2)-N(4)	2.376(9)
Ag(3)-O(2)	2.392(10)		
N(2)-Ag(1)-N(2)#1	161.6(5)	N(2)-Ag(1)-N(3)	69.8(3)
N(2)#1-Ag(1)-N(3)	124.5(3)	N(3)-Ag(1)-N(3)#1	91.8(4)
N(5)#1-Ag(2)-N(5)	161.5(5)	N(5)#1-Ag(2)-N(4)	124.4(3)
N(4)-Ag(2)-N(4)#1	93.3(4)	O(2)-Ag(3)-O(2)#2	128.8(5)

[a] Symmetry transformations used to generate equivalent atoms: #1 -y+1,-x+1,-z+1/6 #2 x,x-y+1,-z-1/6 #3 -x,-x+y,-z+1/3

Table S2. Interatomic Distances (Å) and Bond Angles (deg) for **1’.**

Ag(1)-N(2)	2.239(2)	Ag(1)-N(3)	2.417(2)
Ag(2)-N(5)	2.2217(18)	Ag(2)-N(4)	2.402(2)
Ag(3)-O(2)	2.334(2)	Ag(3)-O(1)#4	2.470(2)
N(2)-Ag(1)-N(2)#1	164.69(12)	N(2)-Ag(1)-N(3)	70.33(8)
N(2)#1-Ag(1)-N(3)	121.80(7)	N(2)-Ag(1)-N(3)#1	121.80(7)
N(2)#1-Ag(1)-N(3)#1	70.33(8)	N(3)-Ag(1)-N(3)#1	88.80(11)
N(5)#1-Ag(2)-N(5)	160.73(13)	N(5)#1-Ag(2)-N(4)	125.21(8)
N(5)-Ag(2)-N(4)	69.94(8)	N(4)-Ag(2)-N(4)#1	91.52(10)
O(2)-Ag(3)-O(2)#2	121.47(7)	O(2)-Ag(3)-O(1)#3	124.25(7)
O(2)#2-Ag(3)-O(1)#3	97.96(6)	O(1)#3-Ag(3)-O(1)#4	88.36(9)

Symmetry transformations used to generate equivalent atoms: #1 -y+1,-x+1,-z+1/6 #2 x,x-y+1,-z-1/6 #3 x-y+1,x+1,z-1/6 #4 x-y+1,-y+1,-z #5 y-1,-x+y,z+1/6 #6 -x,-x+y,-z+1/3

Reference

1. J. He, J.-J. Duan, H.-T. Shi, J. Huang, J.-H. Huang, L. Yu, M. Zeller, A. D. Hunter, Z.-T. Xu, *Inorg. Chem*., advanced article, DOI. 10.1021/ic500677t.

2. (a) L. Alaerts, C. E. A. Kirschhock, M. Maes, M. A. Veen, V. Finsy, A. Depla, J. A. Martens, G. V. Baron, P. A. Jacobs, J. F. M. Denayer, D. E. De Vos, *Angew. Chem. Int. Ed.* 2007, **46**, 4293. (b) K. A. Cychosz, A. G. Wong-Foy, A. J. Matzger, *J. Am. Chem. Soc.* 2008, **130**, 6938.