Supporting information

Does Crystal or Gel Matters to Stereo Chemistry of a Reaction? Silver Complexation Promoted Solid-state [2+2] Reaction of an Unsymmetrical Olefin

Suman Samai, Prabir Ghosh and Kumar Biradha*

General procedure for the preparation of the ligand, **1** and formation of gel with $AgNO_3$ and its characterization with FESEM, TEM and rheology experiment of the gel, isolation of dimmers and their characterization by ^1H NMR, elemental analysis, XRPD pattern of xerogel and Ag(I)complex, ^1H NMR of mechanically grounded sample, IR spectra of all the compounds, UV spectra for gel and xerogel, table for crystallographic parameters, crystal structure determination.

Experimental

Method

FTIR spectra were recorded with a Perkin Elmer Instrument Spectrum Rx Serial No. 73713. Powder XRD patterns were recorded with a BRUKER AXS D8 ADVANCE diffractometer. ^{1}H NMR and spectra were recorded on a BRUKER-AC 200/400 MHz. spectrometer. Elemental analyses were carried out by Perkin Elmer Series II 2400 and melting points were recorded using a Fisher Scientific melting point apparatus cat. No.12-144-1. A field emission scanning electron microscope (FESEM, Zeiss, Supra-40) operating at 5−10 kV was used to obtain the micrograph. The gel materials were examined by a transmission electron microscope (FEI-TECNAI G2 20S-TWIN, Type-5022/22). Rheological measurement was performed on a Bohlin Gemini (Malvern, UK) controlled-stress rheometer using 20 mm diameter parallel plate geometry with a constant tool gap of 200 μm.

Synthesis of 1:

The ligand **1** was synthesized from the condensation reaction of o-phenylenediamine and 4-pyridylacrylic acid in the presence of polyphosphoric acid (PPA) by following a literature procedure.[1] 4-pyridylacrylic acid (2.0 g, 13.4 mmol) and o-phenylenediamine (1.45 g, 13.4 mmol) were added to PPA and mixed thoroughly to make a pasty mass. The mixture was then heated slowly to 190−200 °C and stirred for 2−3 h; the mixture was allowed to cool to about 100 °C. Then, the viscous crude mixture was poured in a thin stream into a large volume of rapidly stirred cold water. The insoluble residue was collected by filtration, washed with water, and reslurried with an aqueous ammonia to make the solution slightly basic (pH 8−9). Again, the solid residue was filtered and washed thoroughly with water until the residue part become base free. The product was dried under vacuum and recrystallized from methanol water mixture (2:1, v/v). Yellow crystalline material was isolated in good yield. Yield 75%; mp = 232-234 °C.

Preparation of gel:

0.1 g of ligand **1** (0.4 mmol) was taken in a vial and dissolved in 5 mL of methanol. With this solution methanolic solution $AgNO_3$ (0.076 g, 0.4 mmol) was mixed. Yellowish colored gel was found to appear immediately after mixing, which is stable in inverted vial. On standing for 5-6 h in room temperature the gel transformed to precipitate, that precipitate converts to good yellow colored crystals after 6-7 days.

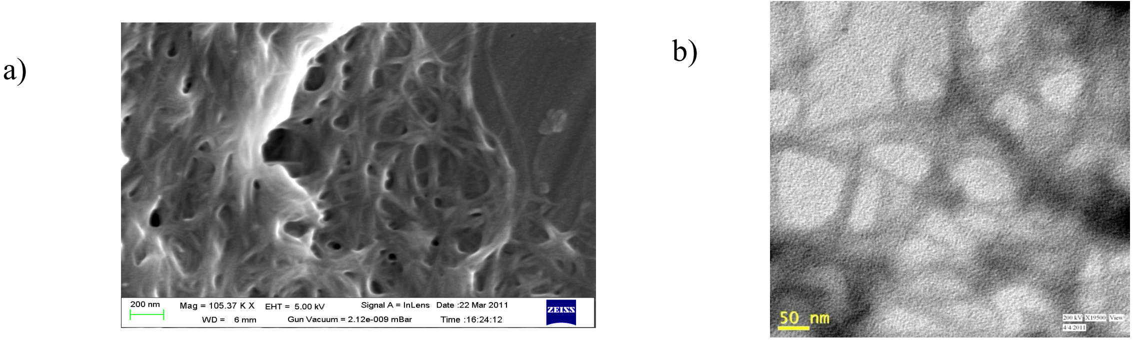

Figure S1 a) FESEM and b) TEM image of the gel derived from ligand **1** and $AgNO_3$

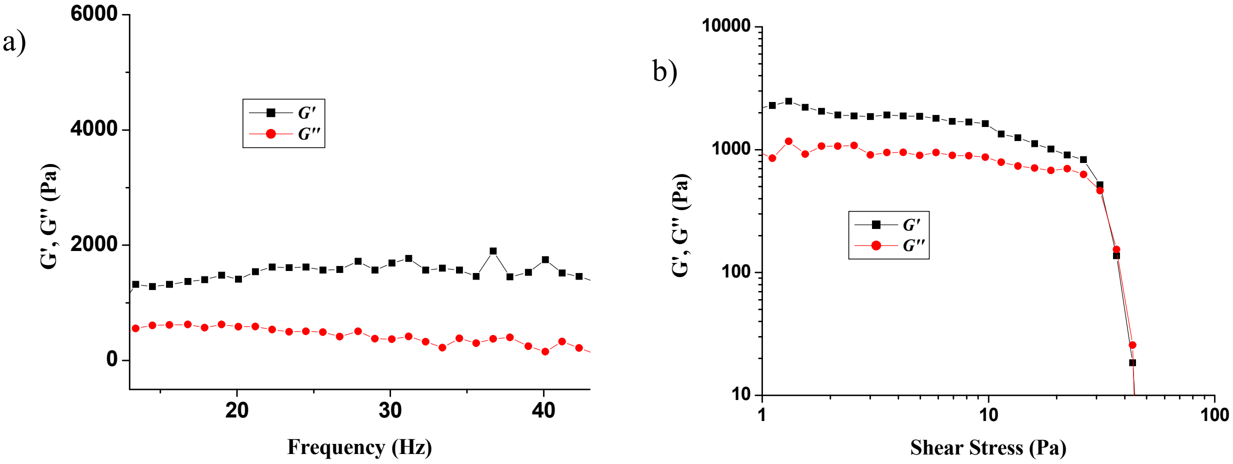

Figure S2 Variation of storage modulus (*G'*) and loss modulus (*G''*) with a) frequency (Hz) and b) shear stress (Pa) of gel derived from **1** and $AgNO_3$

Separation of dimmer 2 by acid-base workup:

About 0.5g of irradiated gel was taken in 5 mL of water and then acidified with dilute HCL up to pH 2-3. The resulted precipitate of AgCl was removed by filtration; the filtrate was carefully neutralized by drop wise addition of NH_4OH. The resulted solid product was isolated by filtering and dried in oven. The crude dimer was crystallized as the needle shaped crystals from THF-toluene (1:2, v/v) mixture. mp= >300°C, Elemental analysis for $C_{35}H_{34}N_6O_2$: Exptl C 73.62%, H 6.10%, N 14.60%; Calcd C 73.66%, H 6.01%, N 14.73%. ^{1}H NMR (D_6DMSO, 400 MHz): δ 12.149 (s, 2H); δ 8.345 (d, *J*=5.6, 4H); δ 7.446-6.991 (12H); δ 5.032 (d, *J*=6.4, 2H); δ 4.779 (d, *J*=6.4, 2H)

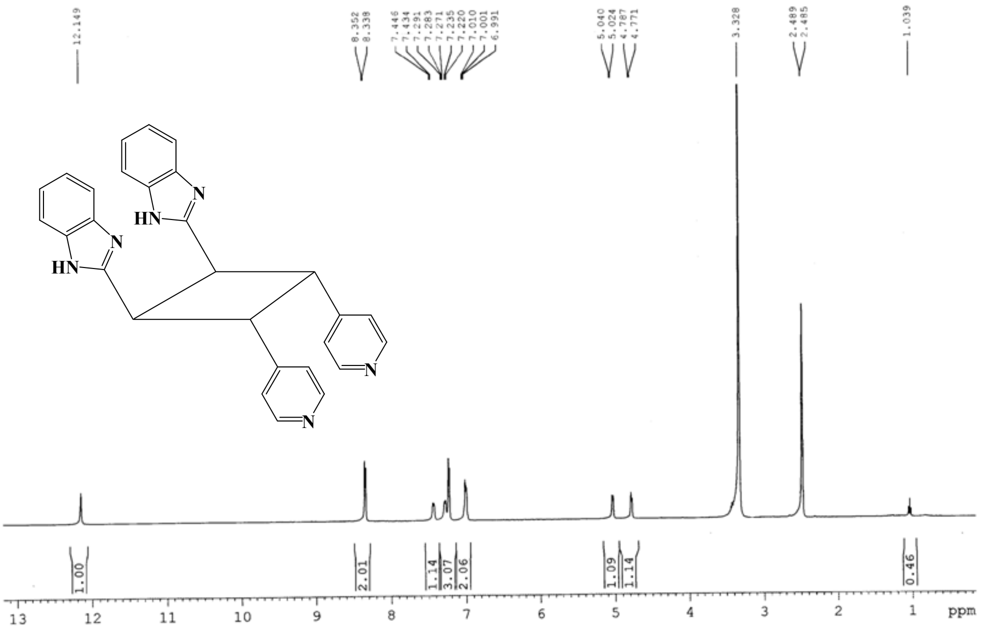

Figure S3 ^{1}H NMR of **2**

Separation of dimmer 4 by acid-base workup:

The procedure is same as described for **2**, the irradiated Ag-complex (**3**) was taken instead of gel and blocked shaped single crystal suitable for X-ray diffraction was grown from MeOH. mp= >300°C, Elemental analysis for $C_{86}H_{90}N_{10}O_{10}$: Exptl C 72.60%, H 6.36%, N 9.90%; Calcd C 72.55%, H 6.37%, N 9.84%. ^{1}H NMR (D_6DMSO, 200 MHz) δ 12.190 (s, 2H); δ 8.276 (d, J= 4.8, 4H); δ 7.492-7.024 (m, 12 H); δ 4.94/4.85 (AA'BB', 4H)

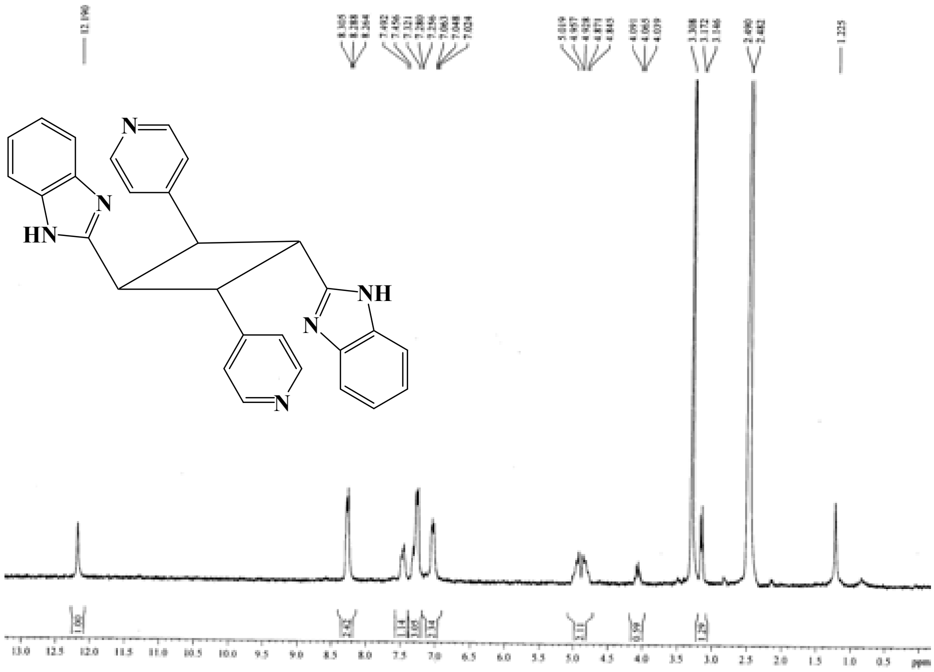

Figure S4 ^{1}H NMR of **4**

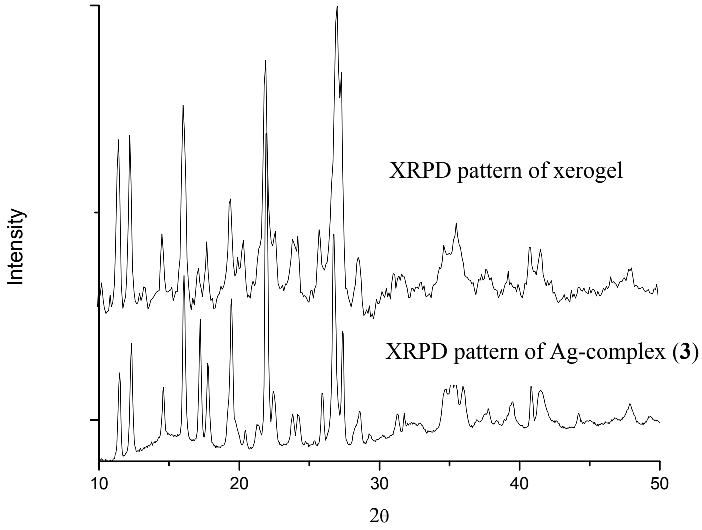

Figure S5 Experimental XRPD pattern of Ag-complex and xerogel

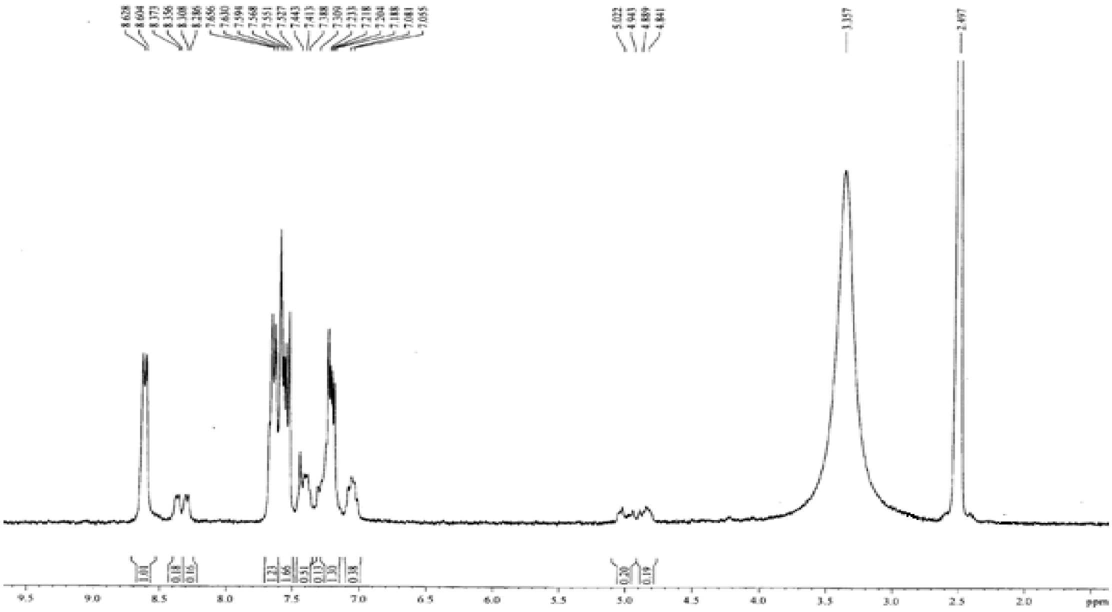

Figure S6 ^{1}H NMR spectra of mechanically grinded sample of **1** with $AgNO_3$ (after free from Ag).

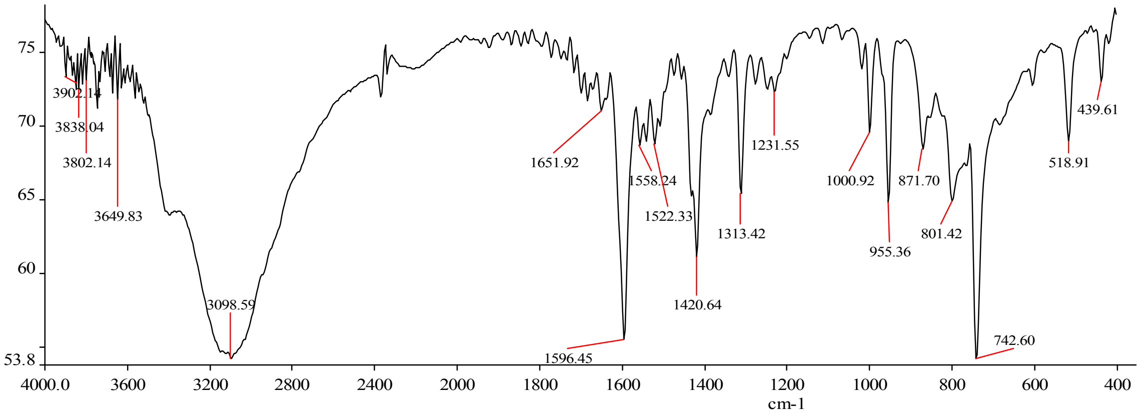

Figure S7 FTIR spectra of **1**.

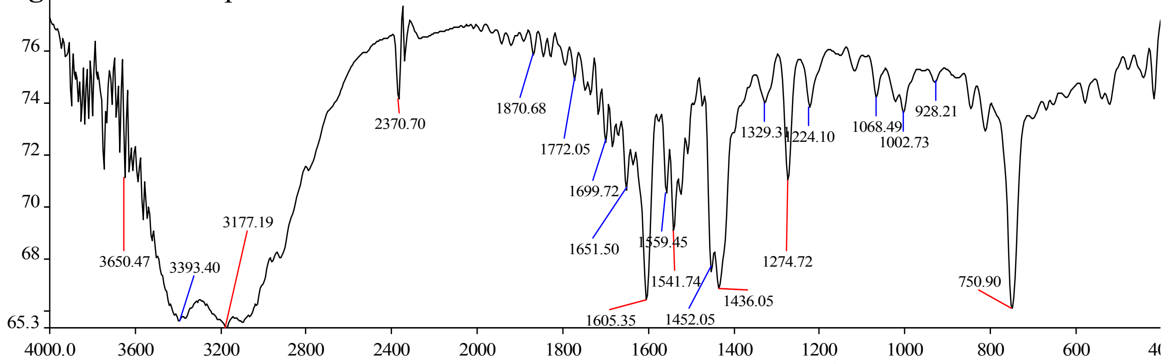

Figure S8 FTIR spectra of **2**.

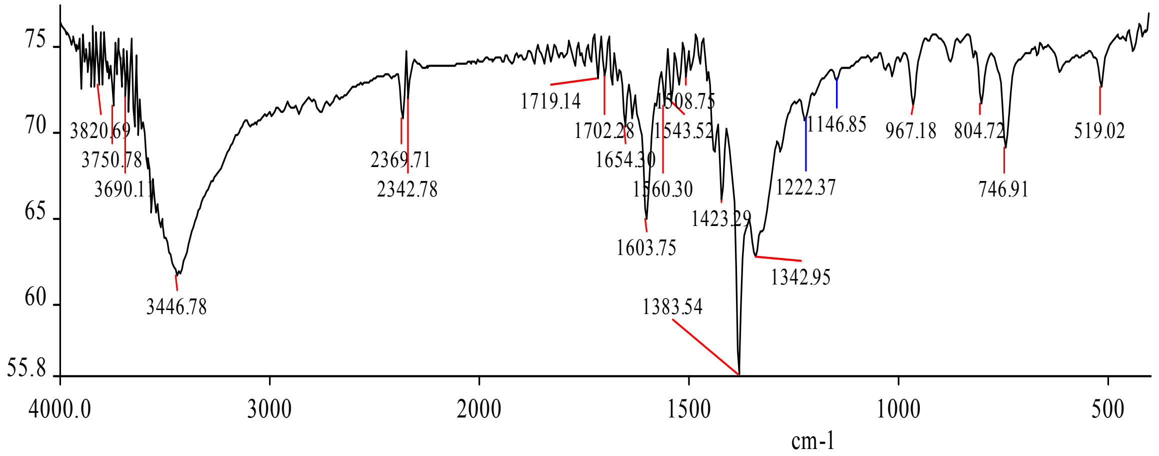

Figure S9 FTIR spectra of **3**.

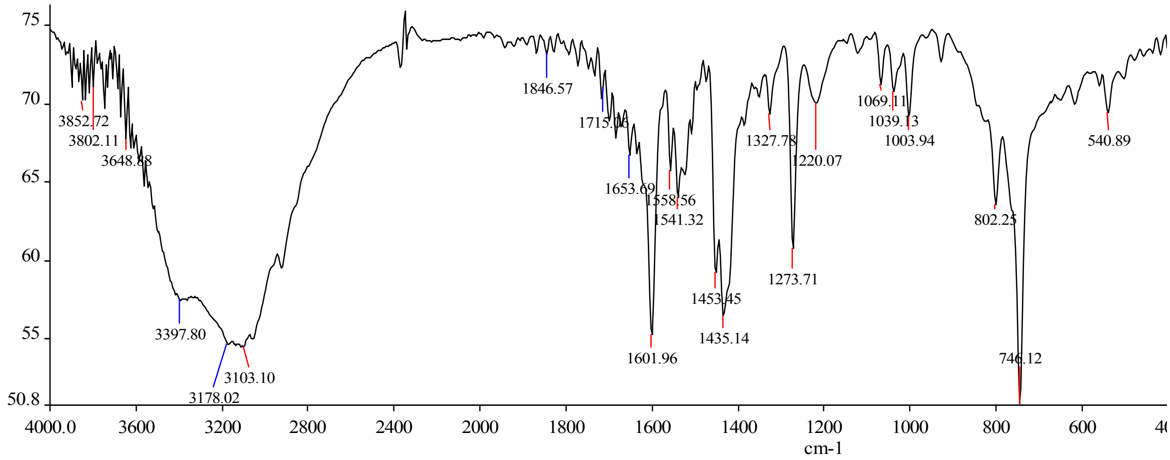

Figure S10 FTIR spectra of **4**.

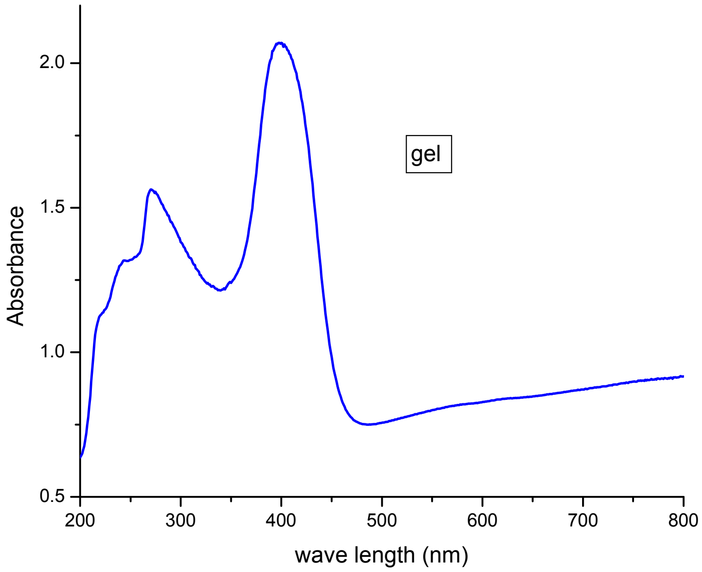

Figure S11 UV-vis spectra of gel derived from **1** and $AgNO_3$.

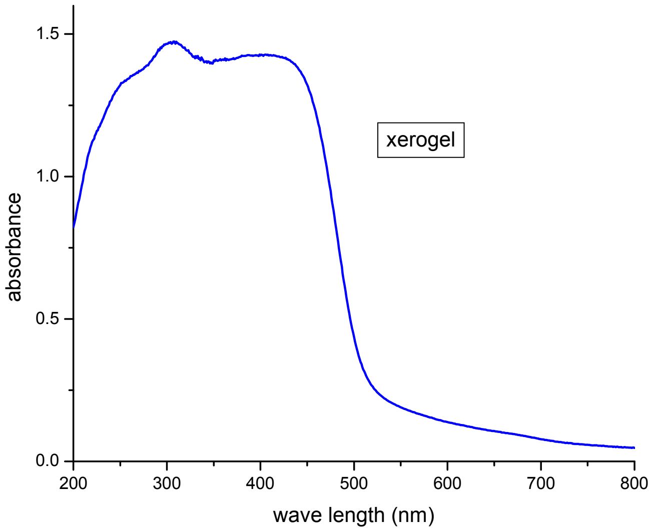

Figure S12 UV-vis spectra of xerogel derived from **1** and $AgNO_3$.

Crystallographic parameters for the crystal structures of **2-4**.

Compound	**2**·toluene·3H_2O	**3**	(**4**)$_3$·8H_2O·2MeOH
Formula	$C_{35}H_{36}N_6O_3$	$C_{15}H_{15}AgN_4O_4$	$C_{86}H_{90}N_{10}O_{10}$
M. Wt.	588.70	423.18	1535.76
T (K)	293(2)	293(2)	293(2)
System	monoclinic	monoclinic	triclinic
Space Group	$P2_1/n$	$P2_1/c$	P-1
a(Å)	10.398(2)	7.750(2)	12.278(2)
b(Å)	12.489(3)	19.835(5)	13.214(2)
c(Å)	24.239(5)	10.502(3)	14.551(2)
α(°)	90.00	90.00	112.161(4)
β(°)	100.067(7)	99.438(9)	90.663(4)
γ(°)	90.00	90.00	112.966(4)
Vol. (Å^3)	3099.2(12)	1592.6(7)	1977.9(4)
Z	4	4	1
D_{calc}(mg/m^3)	1.262	1.765	1.289
R_1 (I>2σ(I))	0.0763	0.0742	0.0604
wR_2 (on F^2, all data)	0.2358	0.1902	0.1965

Crystal Structure Determination: All the single crystal data were collected on a Bruker-APEX-II CCD X-ray diffractometer that uses graphite monochromated Mo Kα radiation (λ=0.71073 Å) at room temperature (293 K) by the hemisphere method. The structures were solved by direct methods and refined by least squares methods on F^2 using SHELX-97.[2] Non-hydrogen atoms were refined anisotropically and hydrogen atoms attached to C-atoms and N-atoms were fixed at calculated positions and refined using a riding model. The H-atoms attached to O-atoms were not included in the final refinement except for MeOH in the structure

(**4**)$_3$·8H_2O·2MeOH, in which H-atom corresponding to MeOH was located and refined using the riding model. In **2**, the toluene molecules are located but highly disordered with distortions in geometry. Therefore in the final refinement, the toluene molecules and one of the water molecule were removed using squeeze option.[3] In Figure 6a, the toluene molecule was taken without anisotropic refinement and also by applying constrains on benzene ring. All these atoms were found to have high thermal parameters.

In **4**, the asymmetric unit has one molecule of **4** (**A**) in a general position and a half (**B**) a molecule of **4** lying about an inversion centre (and thus this molecule has a planar cyclobutane ring). The water molecules form hexameric cyclic water clusters which exhibits chair conformation of cyclohexane. The three O-atoms of water molecules O1W---O3W---O2W form one half of the hexamer, with the other half generated by the inversion-symmetry operation (3-x, 2-y, -1-z). This then leads to O---O Angstrom separations of 2.700(4),[O1W…O3W}; 2.808 (4), [O3W…O2W]; and 2.817(3), O2W…O1W(at 3-x, 2-y, -1-z).

1. M. Hranjec, G. Pavlović, M. Marinović and G. Karminski-Zamola, *Struct. Chem.*, 2008, **19**, 353-359.
2. G. M. Sheldrick, *SHELX-97, Program for the Solution and Refinement of Crystal Structures*; University of Göttingen: Germany, 1997.
3. A. L. Spek, *PLATON A Multi Purpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2002.