Electronic Supplementary Information for Dalton Transactions

Supporting Information

A series of novel organic-inorganic hybrids based on α-$[AlW_{12}O_{40}]^{5-}$ polyoxoanions and transition-metal organoamine complexes

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Crystallography

The crystallographic data of **1-3** were collected at 298 K on the Rigaku R-axis Rapid IP diffractometer using graphite monochromatic Mo-*Kα* radiation (λ = 0.71073 Å) and IP technique. Multi-scan absorption correction was applied. The crystal data were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the *SHELXTL-97* crystallographic software package.[1] During the refinement, heavy atoms (such as W, Al, Ag, Co) can be well anisotropically refined. In the data of **1** and **3**, all the lighter atoms (C and N) on the organic ligands and O atoms derived from the polyoxoanion and solvent water molecules were just isotropically refined due to their unusual thermal parameters with the unisotropical refinement. In the data of **2**, all the lighter atoms (C and N) on the organic ligands were refined isotropically with the O atoms on the polyoxoanions can be anisotropically refined with reasonable thermal parameters. In all three compounds, H atoms on C atoms were fixed on the calculated positions. H atoms on lattice water molecules can not be found from the residual peaks and were directly included in the final molecular formula. The ADDSYM program in PLATON [2] was used to check the space group of **1-3** and no other lower symmetry or unresolved disorder was found, indicating that the refinement of **1-3** was reasonable. In the final refinement, the potential voids in three crystal structures were estimated by the PLATON programme, and only one solvent water molecule should exist in the crystal structure of **1** while the other two data didn't contain any more solvent water molecules. The water molecule in data **1** was directly

included in the final molecule based on the elemental analysis and TG analysis. Furthermore, the data of **1** crystallizes in the chiral space group P1 and refined with the "TWIN" and "BASF" commands to give the flack parameter 0.390(10). In the data of **2**, Ag1 atom should be disordered in three positions (Ag1, Ag1A and its symmetrical operation positions) with 50%, 25% and 25% occupancies, respectively. Further, the deepest hole in Ag(3) position is large, which is due to the series termination errors. Moreover, the polyoxoanion $[AlW_{12}O_{40}]^{5-}$ in **2** was charge-balanced by five Ag+ cations and one H^+ protons. It is initially presumed that the H^+ could reside in the dimeric H_2O clusters with the $[H_5O_2]^+$ form. The distance between two water molecules is ca. 2.8 Å. The detailed crystal data and structure refinement for **1-3** were given in Table 1. Selected bond lengths of 1-3 were listed in Tables S1-S3, respectively.

Reference:

1 G. M. Sheldrick, SHELXL97, *Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997; G. M. Sheldrick, SHELXS97, *Program for Crystal Structure Solution;* University of Göttingen: Göttingen, Germany, 1997.

2 A. L. Spek, PLATON, *A Multipurpose Crystallographic Tool*, Utrecht University: Utrecht, The Netherlands, 1998.

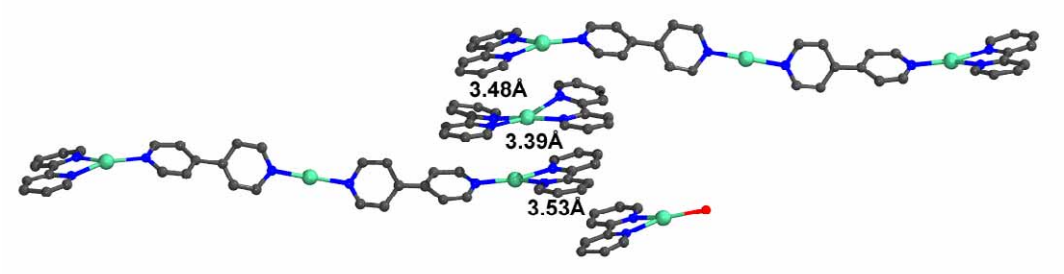

Fig. S1 Ball/stick representation of π-π stacking of organoamine in compound **1**

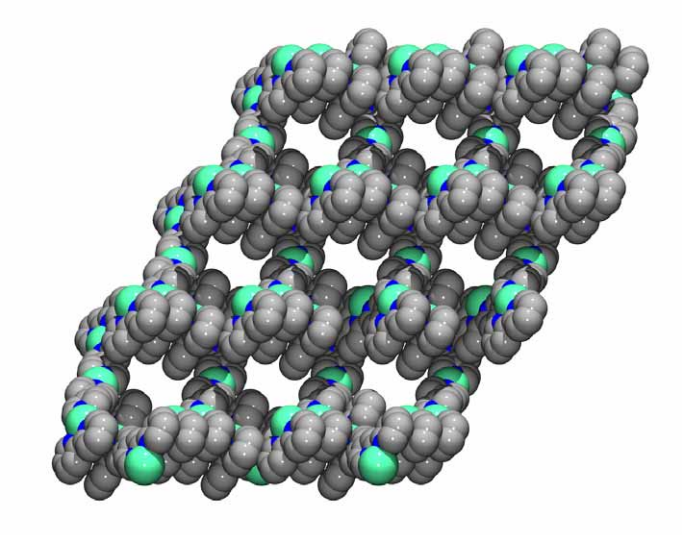

Fig. S2 Space-filling representations of the channels along the *a* axis direction in compound **1**

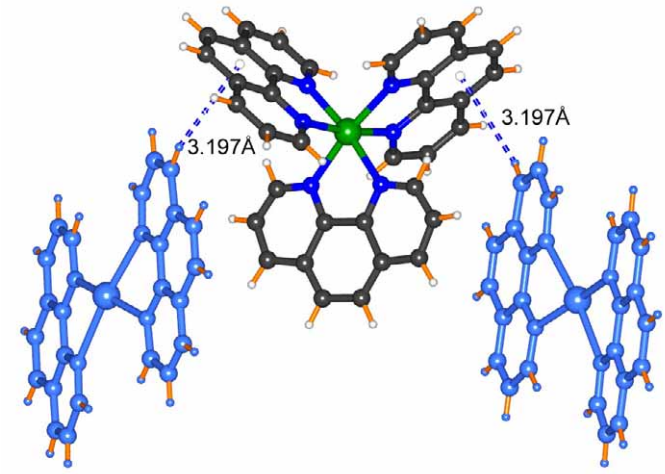

Fig. S3 The C-H…π interactions between the $\{[Ag(phen)_2]_3\}^{3+}$ and $[Ag(phen)_3]^{+}$ of compound **2**

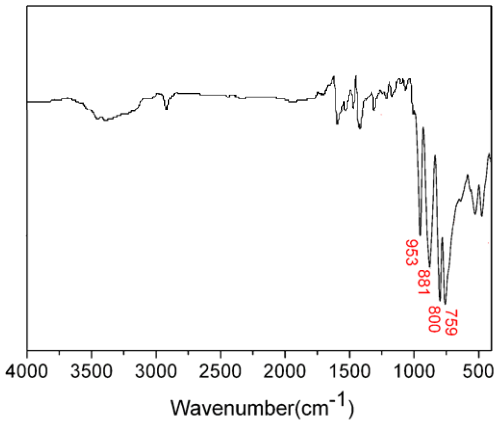

Fig. S4 IR spectra of compound **1**

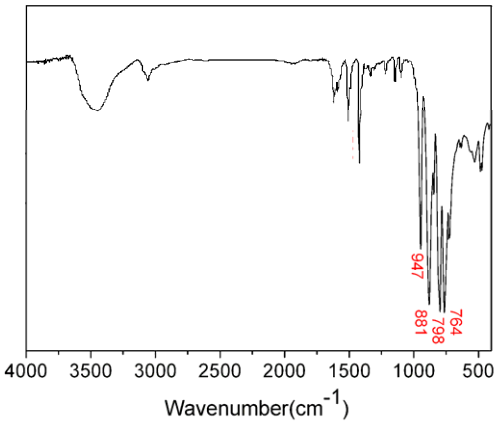

Fig. S5 IR spectra of compound **2**

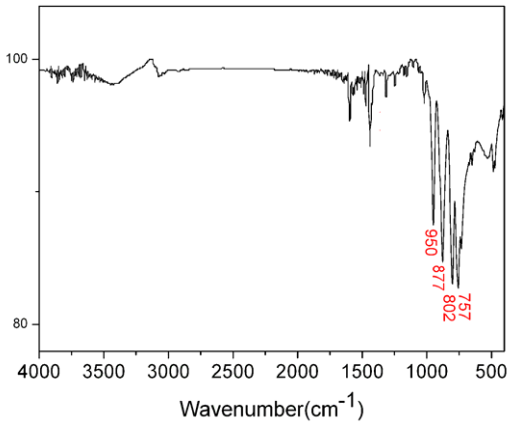

Fig. S6 IR spectra of compound **3**

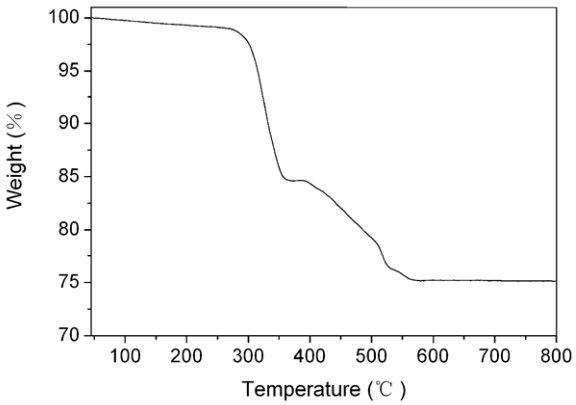

Fig. S7 TG curves of compound **1**.

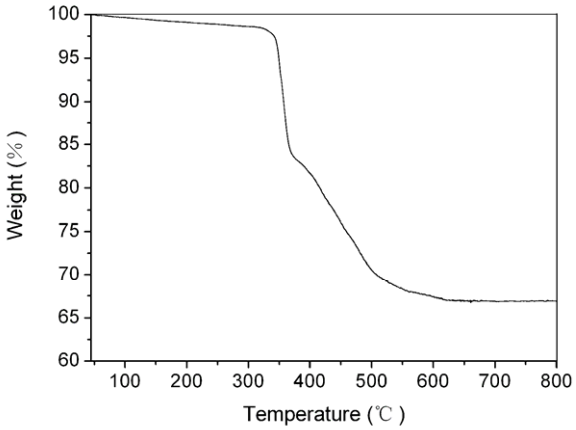

Fig. S8 TG curves of compound **2**.

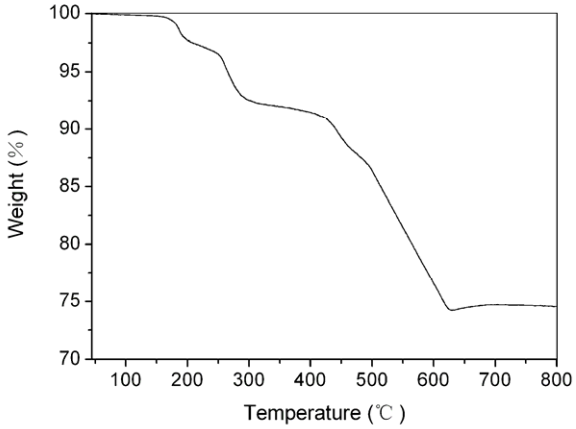

Fig. S9 TG curves of compound **3**.

Table S1. Selected bond lengths (Å) for compound **1**

W(1)-O(1)	1.698(17)	W(1)-O(32)	1.930(12)
W(1)-O(35)	1.865(13)	W(1)-O(4)	1.940(14)
W(1)-O(36)	1.913(12)	W(1)-O(37)	2.238(13)
W(2)-O(9)	1.708(12)	W(2)-O(17)	1.945(13)
W(2)-O(12)	1.879(12)	W(2)-O(32)	1.955(14)
W(2)-O(5)	1.941(15)	W(2)-O(37)	2.287(11)
W(3)-O(8)	1.696(15)	W(3)-O(7)	1.913(13)
W(3)-O(17)	1.902(12)	W(3)-O(4)	1.926(15)
W(3)-O(28)	1.913(11)	W(3)-O(37)	2.262(12)
W(4)-O(11)	1.670(14)	W(4)-O(3)	1.920(13)
W(4)-O(21)	1.899(14)	W(4)-O(14)	1.938(12)
W(4)-O(5)	1.910(14)	W(4)-O(2)	2.281(11)
W(5)-O(19)	1.694(14)	W(5)-O(13)	1.947(12)
W(5)-O(7)	1.910(12)	W(5)-O(6)	1.978(12)
W(5)-O(14)	1.918(11)	W(5)-O(2)	2.290(13)
W(6)-O(20)	1.713(14)	W(6)-O(22)	1.929(14)
W(6)-O(3)	1.904(12)	W(6)-O(34)	1.949(12)
W(6)-O(6)	1.905(13)	W(6)-O(2)	2.240(12)
W(7)-O(40)	1.720(14)	W(7)-O(26)	1.944(13)
W(7)-O(34)	1.849(13)	W(7)-O(27)	1.973(15)
W(7)-O(33)	1.891(14)	W(7)-O(16)	2.253(11)
W(8)-O(18)	1.682(14)	W(8)-O(28)	1.903(11)
W(8)-O(13)	1.891(14)	W(8)-O(26)	1.958(12)
W(8)-O(39)	1.898(16)	W(8)-O(16)	2.279(12)
W(9)-O(23)	1.706(15)	W(9)-O(24)	1.912(14)
W(9)-O(15)	1.890(12)	W(9)-O(31)	1.940(13)
W(9)-O(35)	1.898(13)	W(9)-O(25)	2.277(13)
W(10)-O(30)	1.714(14)	W(10)-O(31)	1.926(15)
W(10)-O(22)	1.863(15)	W(10)-O(29)	1.936(12)
W(10)-O(33)	1.920(13)	W(10)-O(25)	2.262(11)
W(11)-O(10)	1.720(13)	W(11)-O(29)	1.929(12)
W(11)-O(12)	1.914(12)	W(11)-O(24)	1.979(15)
W(11)-O(21)	1.920(15)	W(11)-O(25)	2.263(11)
W(12)-O(38)	1.721(15)	W(12)-O(39)	1.939(15)
W(12)-O(36)	1.882(12)	W(12)-O(27)	1.960(14)
W(12)-O(15)	1.932(13)	W(12)-O(16)	2.257(13)
Ag(1) - O(5)	2.375(14)	Ag(3)-N(9)	2.159(16)
Ag(1)-N(2)	2.373(18)	Ag(3)-N(7)	2.178(19)
Ag(1)-N(1)	2.27(2)	Ag(3)-N(8)	2.36(2)

Ag(2)-N(11)	2.218(16)	Ag(4)-N(12)	2.160(17)
Ag(2)-N(10)	2.159(16)	Ag(4)-N(13)	2.252(16)
Ag(5)-N(6)	2.28(2)	Ag(4)-N(14)	2.35(2)
Ag(5)-N(4)	2.325(19)	Ag(5)-N(5)	2.53(3)
Al(1)-O(25)	1.685(13)	Al(1)-O(37)	1.749(13)
Al(1)-O(2)	1.706(15)	Al(1)-O(16)	1.772(12)

Table S2. Selected bond lengths (Å) for compound **2**

W(1)-O(3)	1.714(8)	W(1)-O(2)	1.950(7)
W(1)-O(1)	1.895(7)	W(1)-O(4)	1.954(7)
W(1)-O(5)	1.910(7)	W(1)-O(9)	2.272(7)
W(2)-O(6)	1.702(7)	W(2)-O(8)	1.916(7)
W(2)-O(7)	1.892(7)	W(2)-O(10)	1.946(7)
W(2)-O(4)	1.912(7)	W(2)-O(9)	2.253(7)
W(3)-O(12)	1.720(7)	W(3)-O(11)	1.932(7)
W(3)-O(2)#1	1.882(7)	W(3)-O(13)	1.956(7)
W(3)-O(14)	1.923(7)	W(3)-O(15)	2.234(7)
W(4)-O(16)	1.712(7)	W(4)-O(1)#1	1.942(7)
W(4)-O(11)	1.897(7)	W(4)-O(5)	1.950(7)
W(4)-O(10)	1.905(7)	W(4)-O(9)	2.261(7)
W(5)-O(20)	1.733(7)	W(5)-O(14)	1.928(7)
W(5)-O(19)	1.899(8)	W(5)-O(7)#1	1.937(7)
W(5)-O(18)	1.907(8)	W(5)-O(15)	2.257(6)
W(6)-O(17)	1.724(8)	W(6)-O(19)#1	1.922(8)
W(6)-O(8)	1.896(7)	W(6)-O(18)	1.946(7)
W(6)-O(13)	1.913(8)	W(6)-O(15)	2.277(7)
Ag(1)-N(1)#2	2.354(12)	Ag(1)-N(2)#2	2.421(13)
Ag(1)-N(1)	2.354(12)	Ag(1)-N(2)	2.421(13)
Ag(1)-Ag(2)	3.313(12)	Ag(1)-Ag(2)#2	3.313(12)
Ag(1A)-N(1)#2	2.36(3)	Ag(1A)-N(2)#2	2.10(3)
Ag(1A)-N(1)	2.40(3)	Ag(1A)-N(2)	2.750(3)
Ag(1A)-Ag(2)	3.24(2)	Ag1(1A)-Ag(2)#2	3.419(2)
Ag(2)-N(4)	2.255(11)	Ag(2)-N(6)	2.471(12)
Ag(2)-N(5)	2.299(11)	Ag(2)-N(3)	2.525(13)
Ag(3)-N(7)	2.072(10)	Ag(3)-N(7)#3	2.072(10)
Ag(3)-N(8)	2.097(10)	Ag(3)-N(8)#3	2.097(10)
Ag(3)-N(9)	2.157(8)	Ag(3)-N(9)#3	2.157(8)
Al(1)-O(9)	1.728(7)	Al(1)-O(15)#1	1.740(7)
Al(1)-O(9)#1	1.728(7)	Al(1)-O(15)	1.740(7)

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

Table S3. Selected bond lengths (Å) for compound **3**

W(1)-O(7)	1.693(12)	W(1)-O(40)	1.943(12)
W(1)-O(26)	1.888(11)	W(1)-O(39)	1.984(12)
W(1)-O(36)	1.890(12)	W(1)-O(15)	2.249(11)
W(2)-O(3)	1.694(12)	W(2)-O(40)	1.908(12)
W(2)-O(35)	1.859(12)	W(2)-O(27)	1.985(12)
W(2)-O(29)	1.898(11)	W(2)-O(15)	2.260(11)
W(3)-O(10)	1.726(12)	W(3)-O(38)	1.919(12)
W(3)-O(39)	1.844(11)	W(3)-O(24)	2.001(13)
W(3)-O(34)	1.888(12)	W(3)-O(16)	2.247(11)
W(4)-O(1)	1.725(13)	W(4)-O(37)	1.953(12)
W(4)-O(31)	1.868(11)	W(4)-O(36)	1.970(11)
W(4)-O(27)	1.882(11)	W(4)-O(15)	2.252(12)
W(5)-O(2)	1.711(14)	W(5)-O(23)	1.944(11)
W(5)-O(21)	1.911(12)	W(5)-O(30)	1.959(11)
W(5)-O(29)	1.911(11)	W(5)-O(33)	2.253(11)
W(6)-O(9)	1.696(12)	W(6)-O(21)	1.934(12)
W(6)-O(13)	1.882(12)	W(6)-O(31)	1.957(11)
W(6)-O(22)	1.884(13)	W(6)-O(33)	2.256(11)
W(7)-O(20)	1.721(13)	W(7)-O(18)	1.949(12)
W(7)-O(12)	1.881(12)	W(7)-O(32)	1.955(12)
W(7)-O(24)	1.882(12)	W(7)-O(16)	2.229(12)
W(8)-O(11)	1.713(13)	W(8)-O(34)	1.955(12)
W(8)-O(18)	1.832(12)	W(8)-O(35)	1.969(11)
W(8)-O(30)	1.872(11)	W(8)-O(16)	2.284(12)
W(9)-O(5)	1.704(13)	W(9)-O(25)	1.949(12)
W(9)-O(14)	1.876(12)	W(9)-O(12)	1.974(12)
W(9)-O(28)	1.884(11)	W(9)-O(17)	2.225(11)
W(10)-O(8)	1.705(13)	W(10)-O(22)	1.931(12)
W(10)-O(37)	1.867(12)	W(10)-O(14)	1.953(12)
W(10)-O(19)	1.902(13)	W(10)-O(17)	2.252(12)
W(11)-O(6)	1.725(12)	W(11)-O(28)	1.928(11)
W(11)-O(32)	1.850(12)	W(11)-O(13)	1.972(12)
W(11)-O(23)	1.902(12)	W(11)-O(33)	2.238(11)
W(12)-O(4)	1.700(12)	W(12)-O(26)	1.927(11)
W(12)-O(25)	1.918(12)	W(12)-O(19)	1.936(13)
W(12)-O(38)	1.920(12)	W(12)-O(17)	2.246(12)
O(20)-Co(1)	2.102(13)	Co(2)-N(24)	2.108(15)
O(2W)-Co(1)	2.130(14)	Co(2)-N(22)	2.121(17)
Co(1)-N(11)	2.079(17)	Co(2)-N(26)	2.124(15)
Co(1)-N(12)	2.102(17)	Co(2)-N(23)	2.136(15)

Co(1)-N(13)	2.103(16)	Co(2)-N(25)	2.158(15)
Co(1)-N(14)	2.107(17)	Co(2)-N(21)	2.164(15)
Co(3)-N(33)#1	2.103(16)	Co(3)-N(32)#1	2.14(2)
Co(3)-N(33)	2.103(16)	Co(3)-N(31)	2.163(16)
Co(3)-N(32)	2.14(2)	Co(3)-N(31)#1	2.163(16)
Al(1)-O(15)	1.726(12)	Al(1)-O(33)	1.737(11)
Al(1)-O(16)	1.734(13)	Al(1)-O(17)	1.744(13)

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