Supporting Information for

# Inorganic-Organic Hybrid Polyoxovanadates Based on $[V_4O_{12}]^{4-}$ or $[VO_3]_2^{2-}$ Clusters: Controllable Synthesis, Crystal Structures and Catalytic Properties in Selective Oxidation of Sulfides

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**Table S1.** Bond valance sum calculations for complexes **1**-**3**.[a][1-3]

| | | | | | |
|---|---|---|---|---|---|
| **1** | **V site** | V1 | V2 | V3 | V4 |
| | **BVS ($V^{IV}$)** | 4.99 | 5.08 | 4.99 | 4.94 |
| | **BVS ($V^{V}$)** | 5.26 | 5.35 | 5.26 | 5.19 |
| | **assigned O.S.** | 5 | 5 | 5 | 5 |
| **2** | **V site** | V1 | V2 | V3 | V4 |
| | **BVS ($V^{IV}$)** | 5.02 | 5.07 | 5.16 | 5.03 |
| | **BVS ($V^{V}$)** | 5.28 | 5.34 | 5.43 | 5.30 |
| | **assigned O.S.** | 5 | 5 | 5 | 5 |
| **3** | **V site** | V1 | V2 | - | - |
| | **BVS ($V^{IV}$)** | 4.78 | 4.85 | - | - |
| | **BVS ($V^{V}$)** | 5.03 | 5.11 | - | - |
| | **assigned O.S.** | 5 | 5 | - | - |

[a] The calculations were performed twice for each individual vanadium atom using bond-valence parameters presented by Brese and O'Keeffe. The oxidation state of atom *i* is given by $\sum v_{ij}=V$ with $v_{ij}=\exp[(R_{ij}-d_{ij})/b]$. Here b is taken to be a 'universal' constant equal to 0.37 Å, $v_{ij}$ is the valence of a bond between two atoms *i* and *j*, $R_{ij}$ is the empirical parameter, and $d_{ij}$ is the observed bond length.

**Table S2.** Selected Bond lengths [Å] and angles [º] for complexes **1**-**3**.

| | | | |
|---|---|---|---|
| | Complex **1** | | |
| Ni(1)-N(1) | 2.081(3) | Ni(1)-N(3) | 2.108(3) |
| Ni(1)-O(1) | 2.033(3) | Ni(2)-N(5) | 2.074(3) |
| Ni(2)-O(2) | 2.068(3) | Ni(2)-O(13) | 2.107(3) |
| Ni(3)-N(7) | 2.111(3) | Ni(3)-N(9) | 2.093(3) |
| Ni(3)-O(6) | 2.028(3) | Ni(4)-O(8) | 2.064(3) |
| Ni(4)-N(13) | 2.090(4) | Ni(4)-N(11) | 2.107(3) |
| V(1)-O(1) | 1.638(3) | V(1)-O(2) | 1.643(3) |
| V(1)-O(3) | 1.773(3) | V(1)-O(4) | 1.778(3) |
| V(2)-O(5) | 1.626(4) | V(2)-O(6) | 1.633(3) |
| V(2)-O(7) | 1.750(4) | V(2)-O(3) | 1.800(3) |
| V(3)-O(9) | 1.628(4) | V(3)-O(8) | 1.639(3) |
| V(3)-O(7) | 1.781(4) | V(3)-O(10) | 1.792(3) |
| V(4)-O(11) | 1.630(3) | V(4)-O(12) | 1.636(3) |
| V(4)-O(10) | 1.783(3) | V(4)-O(4) | 1.812(3) |
| O(1)-Ni(1)-N(1)#1 | 89.21(12) | O(1)-Ni(1)-N(1) | 90.79(12) |
| O(1)-Ni(1)-N(3)#1 | 89.68(12) | N(1)-Ni(1)-N(3)#1 | 87.36(14) |
| O(1)-Ni(1)-N(3) | 90.32(12) | O(2)-Ni(2)-N(5)#2 | 89.10(13) |
| O(2)-Ni(2)-N(5) | 90.90(13) | O(2)-Ni(2)-O(13) | 90.06(11) |
| N(5)-Ni(2)-O(13) | 90.67(12) | O(6)-Ni(3)-N(9)#3 | 89.82(13) |
| O(6)-Ni(3)-N(9) | 90.18(13) | O(6)-Ni(3)-N(7) | 89.52(13) |
| O(8)-Ni(4)-N(13) | 88.54(14) | O(8)#4-Ni(4)-N(13) | 91.46(14) |
| O(1)-V(1)-O(2) | 108.83(14) | O(1)-V(1)-O(3) | 108.64(15) |
| O(1)-V(1)-O(4) | 107.16(14) | O(2)-V(1)-O(4) | 110.87(15) |
| O(5)-V(2)-O(6) | 109.14(18) | O(5)-V(2)-O(7) | 111.1(3) |
| O(5)-V(2)-O(3) | 111.03(16) | O(9)-V(3)-O(8) | 108.42(18) |
| O(8)-V(3)-O(7) | 109.2(2) | O(7)-V(3)-O(10) | 110.60(17) |
| O(11)-V(4)-O(12) | 108.4(2) | O(11)-V(4)-O(10) | 110.57(18) |
| O(11)-V(4)-O(4) | 109.70(18) | V(1)-O(1)-Ni(1) | 176.43(18) |
| V(1)-O(2)-Ni(2) | 155.52(18) | V(1)-O(3)-V(2) | 143.8(2) |
| V(1)-O(4)-V(4) | 133.05(17) | V(2)-O(7)-V(3) | 153.2(2) |
| V(4)-O(10)-V(3) | 137.19(19) | V(3)-O(8)-Ni(4) | 175.45(19) |
| Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z+1; #2 -x+1,-y+1,-z+1; #3 -x+2,-y+1,-z; #4 -x+1,-y+2,-z. | | | |
| | Complex **2** | | |
| Cu(1)-N(1) | 1.999(4) | Cu(1)-N(3) | 2.018(4) |
| Cu(1)-O(1) | 2.422(4) | Cu(2)-N(7) | 1.999(4) |
| Cu(2)-N(5) | 2.015(4) | Cu(3)-N(9) | 1.993(5) |
| Cu(3)-N(11) | 2.032(5) | Cu(3)-O(9) | 2.379(4) |
| Cu(4)-N(15) | 1.999(5) | Cu(4)-N(13) | 2.001(5) |
| V(1)-O(2) | 1.614(4) | V(1)-O(1) | 1.635(4) |
| V(1)-O(4) | 1.797(4) | V(2)-O(6) | 1.600(5) |
| V(2)-O(5) | 1.637(4) | V(2)-O(3) | 1.784(4) |

| | | | |
|---|---|---|---|
| V(2)-O(7) | 1.810(5) | V(3)-O(9) | 1.616(4) |
| V(3)-O(8) | 1.639(4) | V(3)-O(10) | 1.764(4) |
| V(3)-O(7) | 1.769(4) | V(4)-O(11) | 1.617(4) |
| V(4)-O(12) | 1.630(4) | V(4)-O(10) | 1.777(5) |
| V(4)-O(4) | 1.811(4) | N(1)-Cu(1)-N(3)#1 | 90.63(17) |
| N(1)-Cu(1)-N(3) | 89.37(17) | N(1)#1-Cu(1)-O(1) | 88.00(15) |
| N(1)-Cu(1)-O(1) | 92.00(15) | N(3)-Cu(1)-O(1) | 87.20(16) |
| N(7)#2-Cu(2)-N(5) | 89.96(18) | N(7)-Cu(2)-N(5) | 90.04(18) |
| N(5)-Cu(2)-N(5)#2 | 180.0(2) | N(9)-Cu(3)-N(9)#3 | 180.000(1) |
| N(9)-Cu(3)-N(11)#3 | 88.90(19) | N(9)-Cu(3)-N(11) | 91.10(19) |
| N(9)-Cu(3)-O(9)#3 | 89.64(18) | N(9)-Cu(3)-O(9) | 90.36(18) |
| N(11)-Cu(3)-O(9) | 92.83(17) | N(15)-Cu(4)-N(13) | 92.0(2) |
| N(15)-Cu(4)-N(13)#4 | 88.0(2) | O(2)-V(1)-O(1) | 108.0(2) |
| O(2)-V(1)-O(3) | 110.0(2) | O(1)-V(1)-O(3) | 109.2(2) |
| O(1)-V(1)-O(4) | 111.4(2) | O(3)-V(1)-O(4) | 109.13(17) |
| O(6)-V(2)-O(5) | 111.6(3) | O(6)-V(2)-O(3) | 111.3(2) |
| O(5)-V(2)-O(3) | 107.78(19) | O(6)-V(2)-O(7) | 110.7(3) |
| O(9)-V(3)-O(8) | 106.8(2) | O(9)-V(3)-O(10) | 111.0(3) |
| O(8)-V(3)-O(10) | 109.4(3) | O(9)-V(3)-O(7) | 111.1(2) |
| O(8)-V(3)-O(7) | 107.1(2) | O(10)-V(3)-O(7) | 111.2(2) |
| O(11)-V(4)-O(12) | 106.9(3) | O(11)-V(4)-O(10) | 109.3(3) |
| O(12)-V(4)-O(10) | 113.2(3) | O(11)-V(4)-O(4) | 110.7(2) |
| O(12)-V(4)-O(4) | 106.7(2) | O(10)-V(4)-O(4) | 109.9(2) |
| V(1)-O(1)-Cu(1) | 170.0(2) | V(2)-O(3)-V(1) | 135.2(2) |
| V(1)-O(4)-V(4) | 137.5(2) | V(3)-O(7)-V(2) | 137.9(3) |
| V(3)-O(9)-Cu(3) | 169.7(3) | V(3)-O(10)-V(4) | 154.6(4) |

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1; #2 -x+2,-y,-z+1; #3 -x+1,-y+2,-z; #4 -x+1,-y+1,-z.

Complex **3**

| | | | |
|---|---|---|---|
| Co(1)-N(1) | 2.045(2) | Co(1)-O(5)#1 | 2.0662(16) |
| Co(1)-O(2)#2 | 2.0687(16) | Co(1)-O(2)#3 | 2.1283(16) |
| Co(1)-O(7) | 2.1498(17) | Co(1)-O(6) | 2.1522(16) |
| V(1)-O(3) | 1.5951(17) | V(1)-O(2) | 1.7073(16) |
| V(1)-O(4) | 1.8041(16) | V(1)-O(1) | 1.8071(17) |
| V(2)-O(5) | 1.6519(16) | V(2)-O(6) | 1.6738(16) |
| V(2)-O(1) | 1.7623(16) | V(2)-O(4)#3 | 1.7807(16) |
| N(1)-Co(1)-O(5)#1 | 92.46(7) | N(1)-Co(1)-O(2)#2 | 97.67(7) |
| N(1)-Co(1)-O(2)#3 | 177.00(7) | N(1)-Co(1)-O(7) | 91.70(8) |
| O(5)#1-Co(1)-O(7) | 89.56(7) | N(1)-Co(1)-O(6) | 96.37(7) |
| O(2)#2-Co(1)-O(6) | 91.70(6) | O(7)-Co(1)-O(6) | 171.59(6) |
| O(3)-V(1)-O(2) | 108.04(8) | O(3)-V(1)-O(4) | 106.55(9) |
| O(2)-V(1)-O(4) | 108.21(8) | O(3)-V(1)-O(1) | 106.73(8) |
| O(2)-V(1)-O(1) | 113.35(8) | O(4)-V(1)-O(1) | 113.60(8) |
| O(5)-V(2)-O(6) | 110.89(8) | O(5)-V(2)-O(1) | 111.65(8) |
| O(6)-V(2)-O(1) | 108.86(8) | O(5)-V(2)-O(4)#3 | 109.18(8) |
| O(1)-V(2)-O(4)#3 | 108.16(8) | V(2)-O(1)-V(1) | 150.80(10) |
| V(1)-O(2)-Co(1)#2 | 138.38(9) | V(1)-O(2)-Co(1)#4 | 118.02(8) |
| V(2)#4-O(4)-V(1) | 131.53(9) | V(2)-O(5)-Co(1)#5 | 140.71(10) |
| V(2)-O(6)-Co(1) | 126.36(8) | | |

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

**Figure S1.** The $[Co_2O_2]$ square plane structure unit in complex **3**.

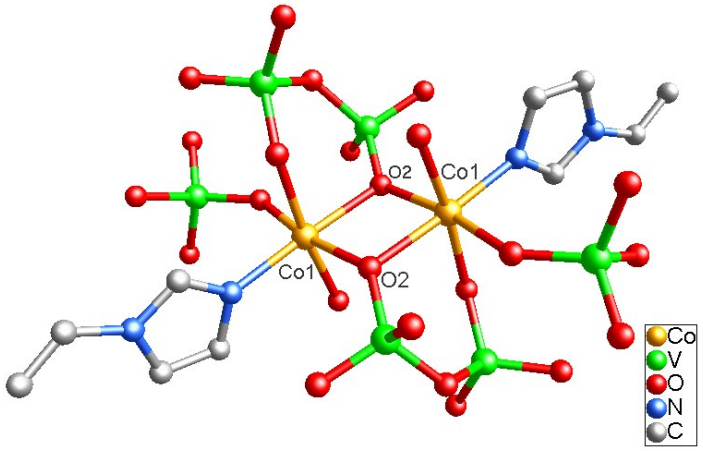



**Figure S2.** The FT-IR spectra of complex **1**.

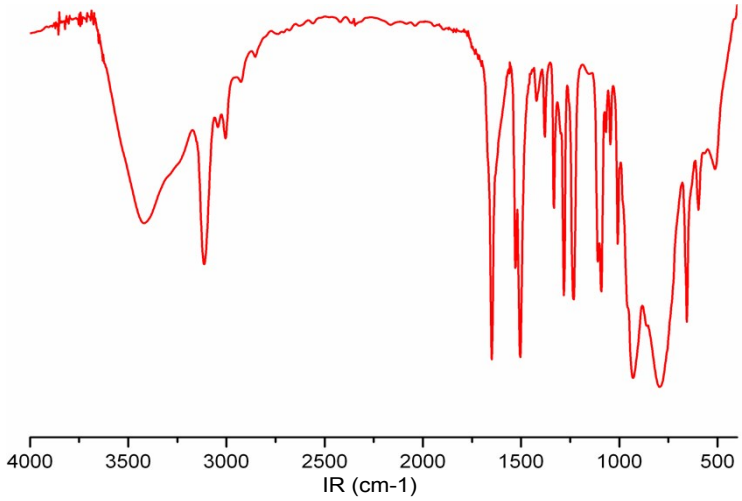



**Figure S3.** The FT-IR spectra of complex **2**.

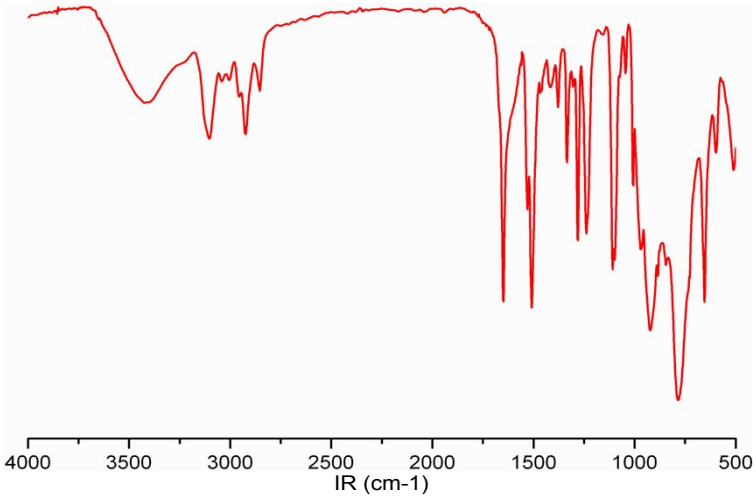


**Figure S4.** The FT-IR spectra of complex **3**.

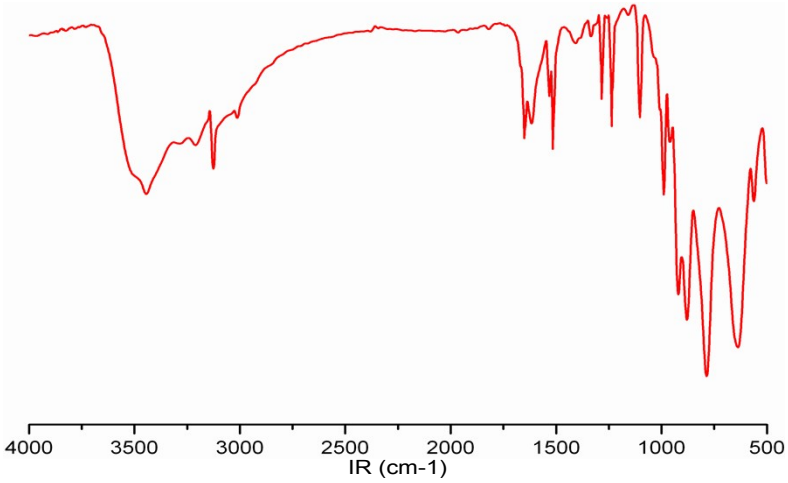



**Figure S5.** The FT-IR spectra of complex **1** after each catalytic cycle.

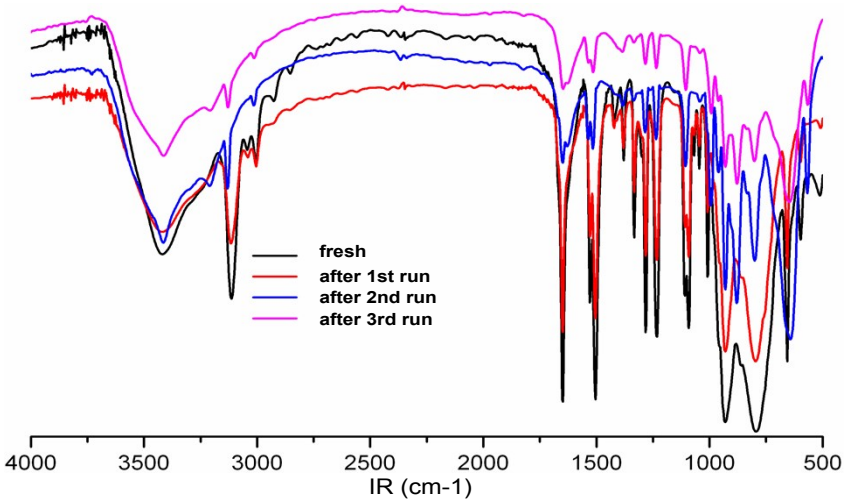



**Figure S6.** The simulated, experimental and after three catalytic cycles PXRD patterns of complex **1**. Simulation based on the SXRD data.

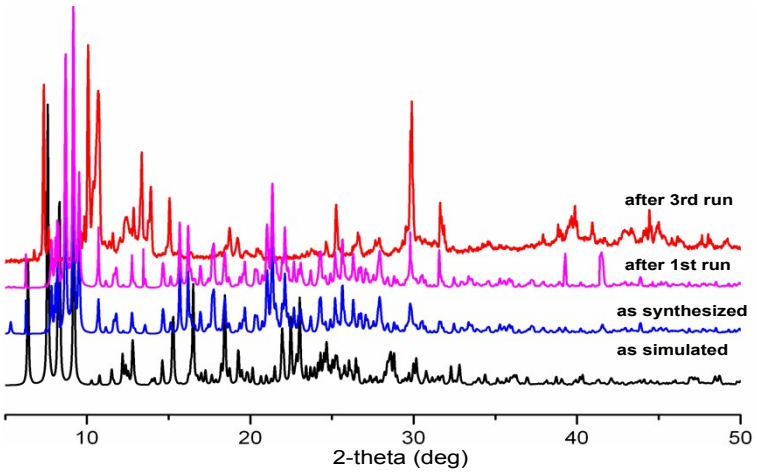


**Figure S7.**The simulated (black) and experimental (red) PXRD patterns of complex **2**. Simulation based on the SXRD data.

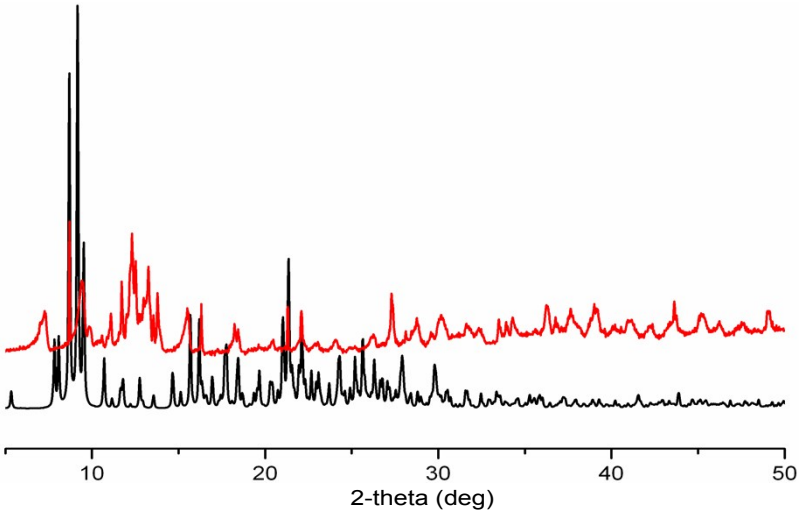
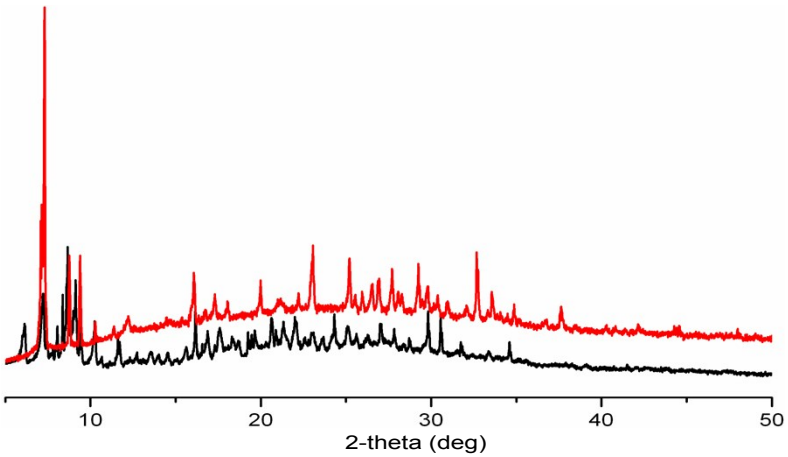



**Figure S8.**The simulated (black) and experimental (red) PXRD patterns of complex **3**. Simulation based on the SXRD data.




**S9.** Atomic absorption analysis of product solution after three catalytic cycles.

The detection limit of the inductively coupled plasma spectrometer (ICP-AES) on a SPECTRO ARCOS EOP analyzer is 0.002mg/L.

**Figure S10**. The crystal structure of $Ni(1\text{-}vIM)_4Cl_2$ (CCDC No. 1881006).

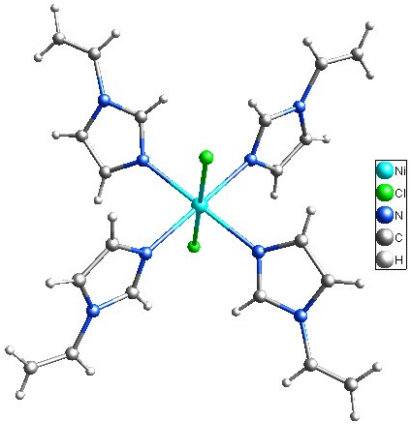
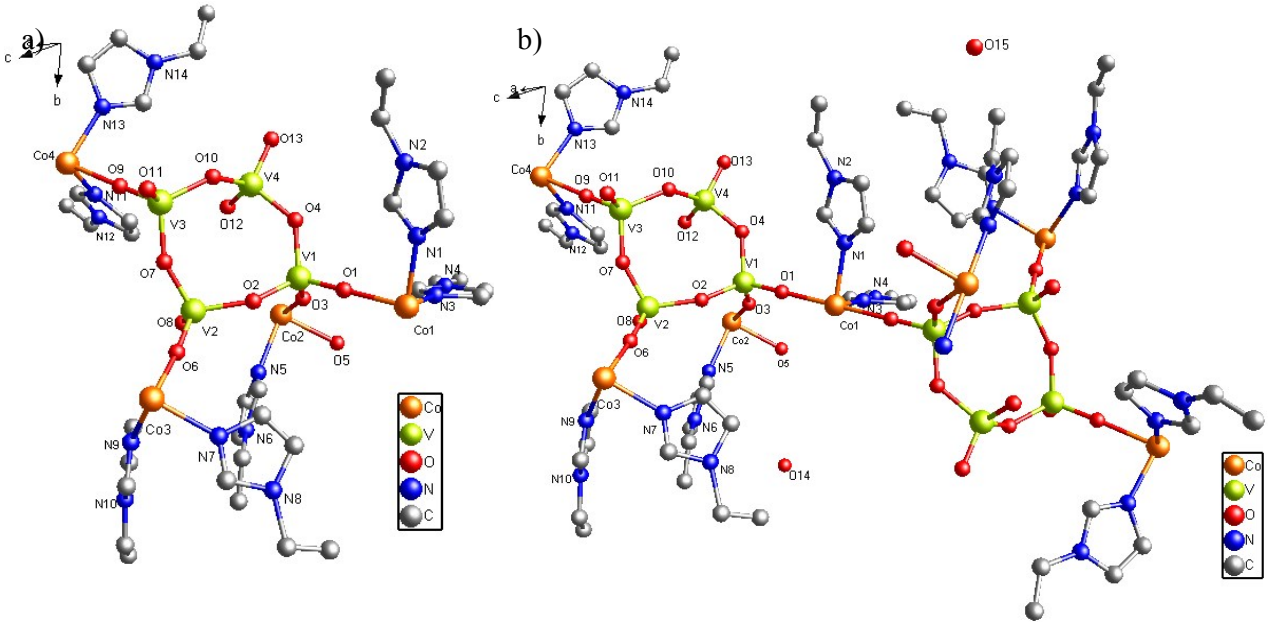


**Figure S11**. The crystal structure of complex $[Co_4(1\text{-vIM})_{14}][V_4O_{12}]_2\cdot 6H_2O$ **(4)** (CCDC No. 1887006). a) Asymmetrical structural unit; b) Molecular structure.




**S12.** The crystallographic data of complex $[Co_4(1\text{-vIM})_{14}][V_4O_{12}]_2\cdot 6H_2O$ **(4)**.

Formula: $C_{70}H_{95}N_{28}O_{30}Co_4V_8$; $M_r$=2451.97; Crystal system: Triclinic; Space group: *P-1*; $a$=12.76(3) Å, $b$=15.37(3) Å, $c$=16.00(3) Å; $\alpha$=68.37(3), $\beta$=66.71(3), $\gamma$=73.74(3); $V$=2644(9) Å$^3$; $Z$=1; $\rho$=1.540 g cm$^{-3}$; $T$=298(2) K; $R_1$=0.0874; $wR_2$=0.1651; $GOF(F^2)$=0.820. More crystallographic data please check the Cambridge Crystallographic Data Centre (CCDC) with entry 1887006.

**Reference:**


[1] N. E. Brese and M. O'Keeffe, *Acta Cryst. Sect. B,* 1991, **47**, 192.

[2] Brown, I. D.; Altermatt, D. *Acta. Cryst.* **1985**, *B41*, 244-247.

[3] Thorp, H. H. *Inorg. Chem.* **1992**, *31*, 1585-1588.