Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Copper-Containing Hybrid Compounds Based on Extremely Rare $[V_2Mo_6O_{26}]^{6-}$ POM as Water Oxidation Catalysts

Halyna I. Buvailo [1], Valeriya G. Makhankova [1,*], Vladimir N. Kokozay [1], Irina V. Omelchenko [2], Svitlana V. Shishkina [2], Julia Jezierska [3], Mariia V. Pavliuk [4], Sergii I. Shylin [4,*]

[1] Department of Chemistry, Taras Shevchenko National University of Kyiv, Volodymyrska 64/13, 01601 Kyiv, Ukraine. E-mail: leram@univ.kiev.ua

[2] Institute for Single Crystals, National Academy of Sciences of Ukraine, Nauky Ave 60, 61001 Kharkiv, Ukraine

[3] Faculty of Chemistry, University of Wroclaw, F. Joliot-Curie 14, 50-383 Wroclaw, Poland

[4] Department of Chemistry – Ångström Laboratory, Uppsala University, P.O. Box 523, 75120 Uppsala, Sweden. E-mail: sergii.shylin@kemi.uu.se

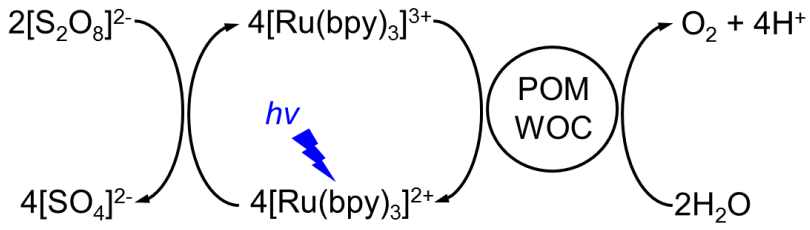


Figure S1. Scheme showing photocatalytic cycle of water oxidation to dioxygen by persulfate with $[Ru(bpy)_3]^{2+}$ as photosensitizer and POM as water oxidation catalyst.

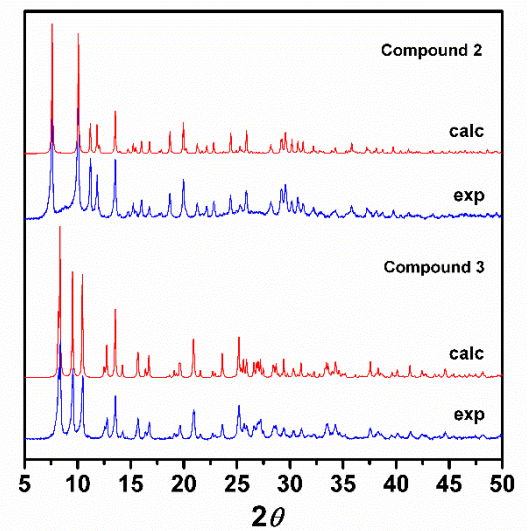


Figure S2. Experimental (red) and calculated (blue) X-ray powder diffraction patterns.

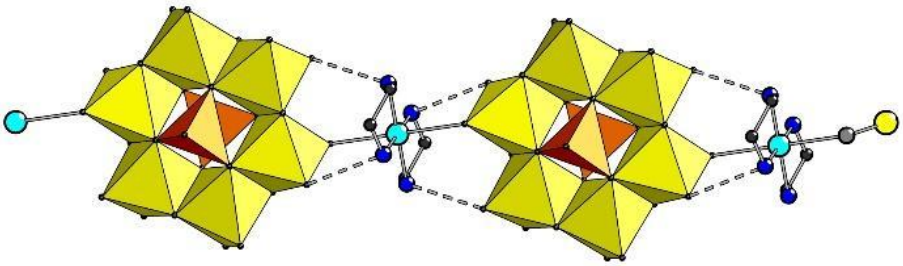


Figure **S3.** Combined polyhedral and ball-and-stick representation of the **1**. The H-bonds are shown as dashed lines. H atoms are omitted for clarity.

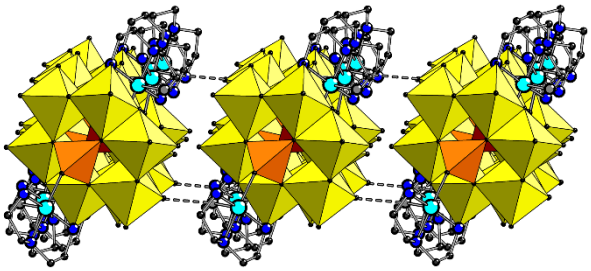


Figure S4. Combined polyhedral and ball-and-stick representation of the H-bonded structure in **2**. The H-bonds are shown as dashed lines. H atoms, non-coordinated water molecules and ammonium cations are omitted for clarity.

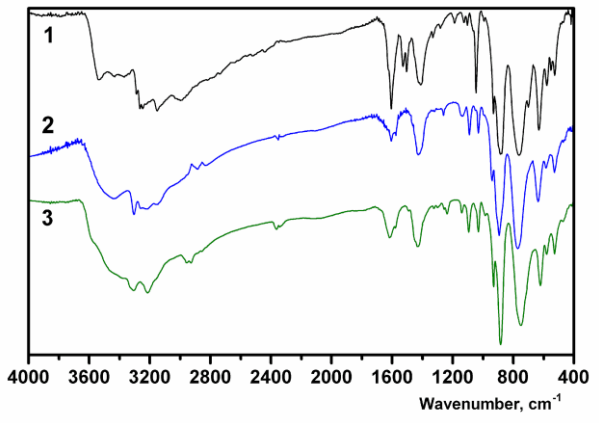
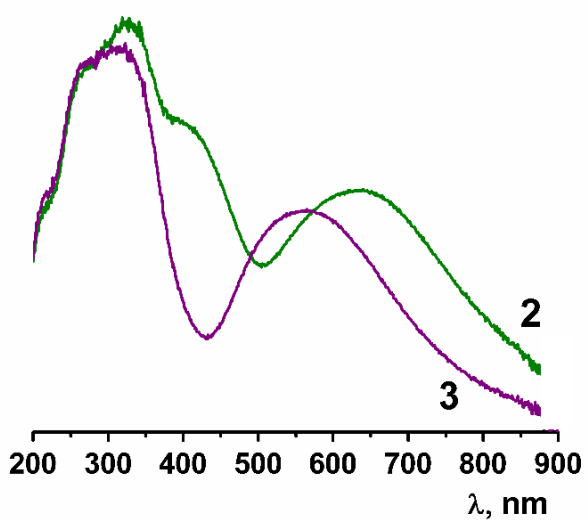
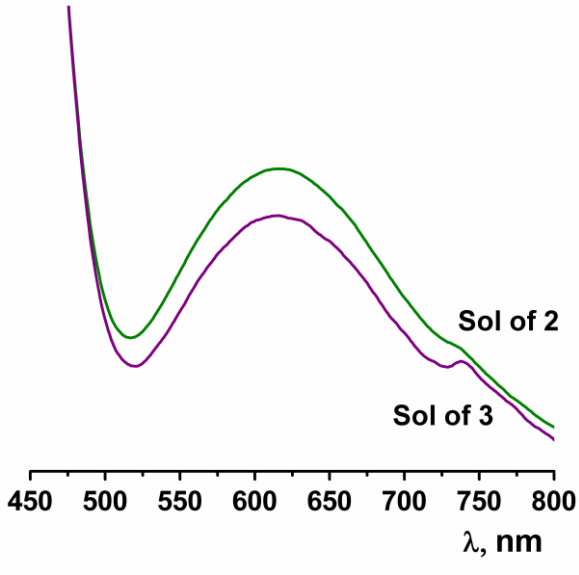


Figure S5. FTIR spectra of **1**–**3** recorded in KBr pellets.



a)



b)

Figure S6. UV-vis reflectance spectra of powdered samples **2** and **3** (a); UV-vis absorption spectra of aqueous solutions of **2** and **3** (b).

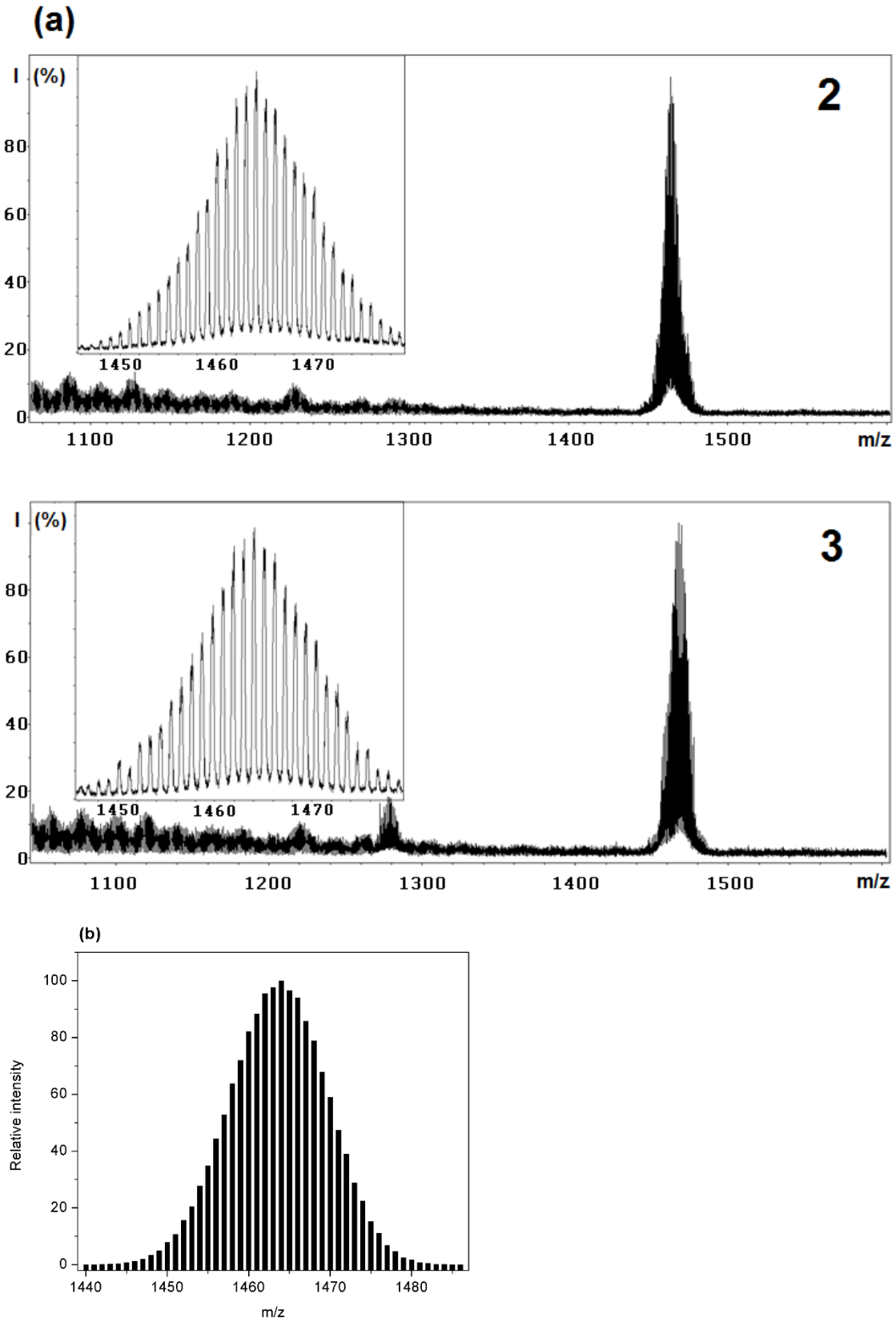
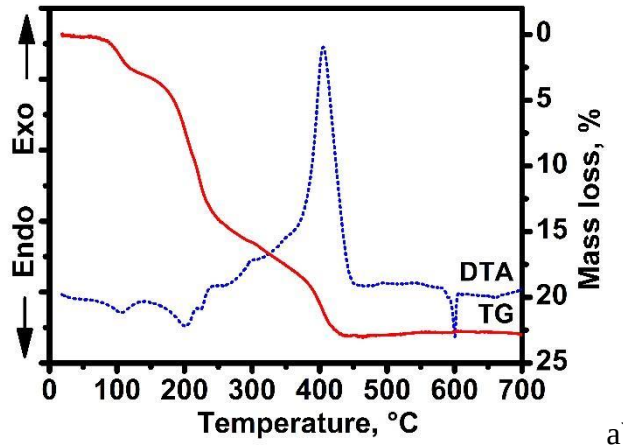
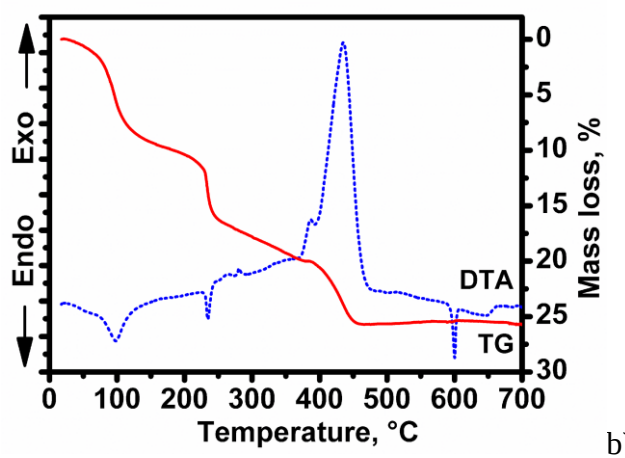


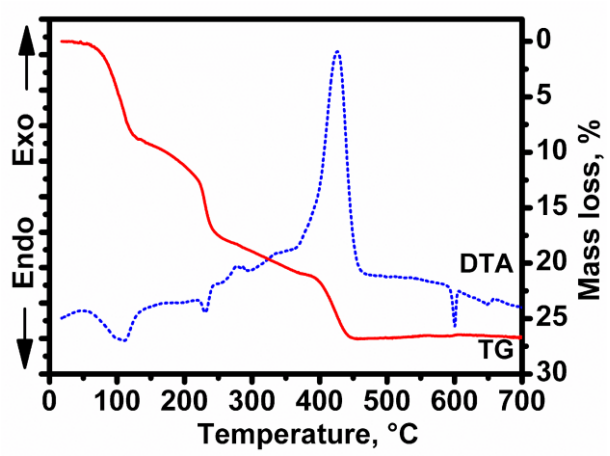
Figure S7. (a) ESI-TOF mass spectra of **2** and **3** (10 μM) in buffered water (borate buffer, 0.1 mM, pH 8.0) obtained in the negative ionization mode. The peak at m/z = 1464 for both **2** and **3** corresponds to $\{[Cu(dien)(H_2O)]_2[\alpha\text{-}V_2Mo_6O_{26}]+H\}^-$. The additional peak at m/z = 1281 for the sample **3** is assigned to $\{[Cu(dien)(H_2O)][\alpha\text{-}V_2Mo_6O_{26}]+3H\}^-$. (b) Calculated isotope pattern for the anion $\{[Cu(dien)(H_2O)]_2[\alpha\text{-}V_2Mo_6O_{26}]+H\}^-$ based on the natural abundance of corresponding isotopes.



a)



b)



c)

Figure S8. TG (solid red) and DTA (dashed blue) curves for **1** (a), **2** (b), **3** (c) recorded in air.

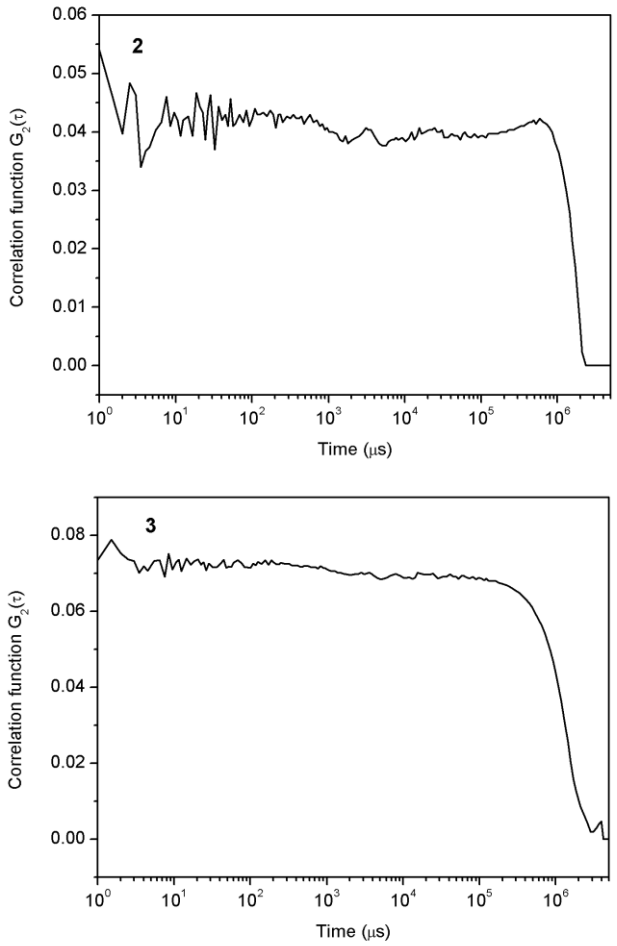


Figure S9. Dynamic light scattering (DLS) correlation functions $G_2(\tau)$ for the solutions containing $[Ru(bpy)_3]^{2+}$, $S_2O_8^{2-}$, and catalyst **2** (top) or **3** (bottom) in borate buffer (pH 8.0) recorded after photocatalysis. No particles are observed since y-interception of $G_2(\tau)$ << 1. The size measurement range was 1 nm – 10 μm.

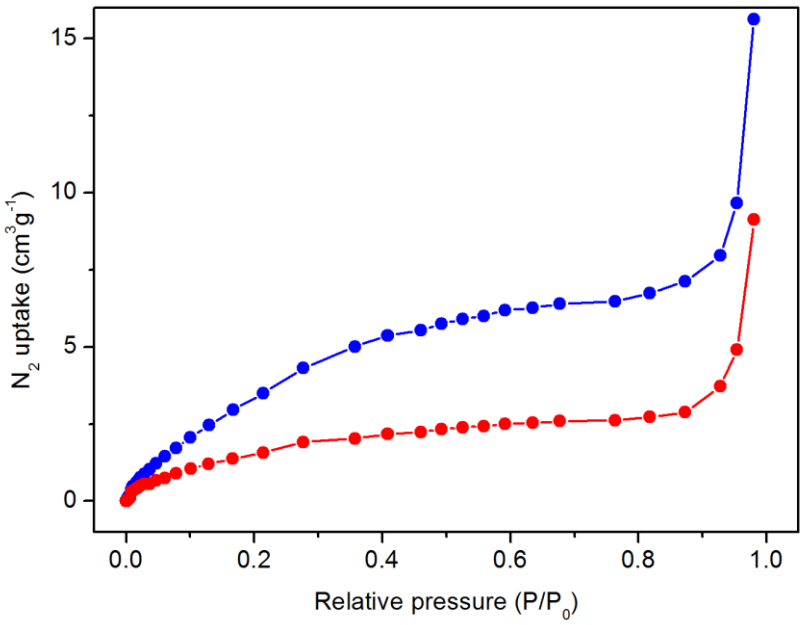


Figure S10. N_2 adsorption isotherms obtained for **2-ox** (red) and **3-ox** (blue) at 77 K.

Table S1. Selected bond distances (Å) and angles (º)

Compound **1**

Bond	distance, Å	Bond	distance, Å
Mo1–O1	1.919(3)	Mo3–O10	1.715(4)
Mo1–O2	1.711(3)	Mo3–O11	2.270(3)
Mo1–O3	1.709(4)	Mo3–O1^{1}	1.921(3)
Mo1–O4	1.930(3)	Mo3–O13^{1}	2.359(4)
Mo1–O5	2.289(4)	Cu1–O7	2.563(3)
Mo1–O11^{1}	2.341(3)	Cu1–N1	1.993(5)
Mo2–O4	1.895(3)	Cu1–N2	2.021(5)
Mo2–O5	2.291(3)	Cu1–O7^{2}	2.563(3)
Mo2–O6	1.717(3)	Cu1–N1^{2}	1.993(5)
Mo2–O7	1.723(4)	Cu1–N2^{2}	2.021(5)
Mo2–O8	1.923(4)	V1–O5	1.755(3)
Mo2–O13^{1}	2.332(3)	V1–O11	1.752(3)
Mo3–O8	1.887(3)	V1–O12	1.634(4)
Mo3–O9	1.709(4)	V1–O13	1.743(3)
angle	°	angle	°
O1–Mo1–O2	98.19(16)	O7–Mo2–O13^{1}	87.88(13)
O1–Mo1–O3	100.31(15)	O8–Mo2–O13^{1}	74.27(13)
O1–Mo1–O4	149.64(14)	O8–Mo3–O9	99.43(15)
O1–Mo1–O5	83.25(14)	O8–Mo3–O10	98.16(15)
O1–Mo1–O11^{1}	73.45(13)	O8–Mo3–O11	82.33(13)
O2–Mo1–O3	104.37(17)	O1^{1}–Mo3–O8	150.12(14)
O2–Mo1–O4	102.44(15)	O8–Mo3–O13^{1}	74.21(13)
O2–Mo1–O5	91.32(15)	O9–Mo3–O10	104.78(18)
O2–Mo1–O11^{1}	164.06(17)	O9–Mo3–O11	164.90(16)
O3–Mo1–O4	95.89(16)	O1^{1}–Mo3–O9	97.55(15)
O3–Mo1–O5	163.12(14)	O9–Mo3–O13^{1}	90.67(16)
O3–Mo1–O11^{1}	90.64(13)	O10–Mo3–O11	89.71(16)
O4–Mo1–O5	74.31(14)	O1^{1}–Mo3–O10	101.05(15)
O4–Mo1–O11^{1}	80.91(12)	O10–Mo3–O13^{1}	163.84(15)
O5–Mo1–O11^{1}	74.44(11)	O1^{1}–Mo3–O11	75.13(13)
O4–Mo2–O5	74.86(14)	O11–Mo3–O13^{1}	75.30(12)
O4–Mo2–O6	101.06(15)	O1^{1}–Mo3–O13^{1}	81.20(13)
O4–Mo2–O7	98.46(16)	O7–Cu1–N1	91.02(14)
O4–Mo2–O8	149.85(14)	O7–Cu1–N2	84.37(14)
O4–Mo2–O13^{1}	83.03(12)	O7–Cu1–O7^{2}	180.00
O5–Mo2–O6	92.41(15)	O7–Cu1–N1^{2}	88.98(14)
O5–Mo2–O7	163.19(13)	O7–Cu1–N2^{2}	95.63(14)
O5–Mo2–O8	80.53(14)	N1–Cu1–N2	85.40(19)
O5–Mo2–O13^{1}	76.11(12)	O7^{2}–Cu1–N1	88.98(14)
O6–Mo2–O7	104.10(16)	N1–Cu1–N1^{2}	180.00
O6–Mo2–O8	97.08(17)	N1–Cu1–N2^{2}	94.60(19)
O6–Mo2–O13^{1}	166.48(17)	O7^{2}–Cu1–N2	95.63(14)
O7–Mo2–O8	100.23(16)	N1^{2}–Cu1–N2	94.60(19)
N2–Cu1–N2^{2}	180.00	O7^{2}–Cu1–N1^{2}	91.02(14)
O7^{2}–Cu1–N2^{2}	84.37(14)	N1^{2}–Cu1–N2^{2}	85.40(19)

O5–V1–O11	112.64(16)	O5–V1–O12	110.33(16)
O5–V1–O13	110.55(16)	O11–V1–O12	106.42(17)
O11–V1–O13	108.81(15)		

[1] 1-x,1-y,2-z; [2] 1-x,-y,1-z

Compound **2**

Bond	distance, Å	Bond	distance, Å
Mo1–O3	2.312(5)	Mo3–O11	1.709(5)
Mo1–O5	1.703(6)	Mo3–O12	1.921(5)
Mo1–O6	1.699(5)	Mo3–O13	1.695(5)
Mo1–O7	1.915(6)	Mo3–O4[1]	2.336(6)
Mo1–O2[1]	2.319(5)	Cu1–O1	1.984(5)
Mo1–O12[1]	1.914(5)	Cu1–O1S	2.382(7)
Mo2–O3	2.348(5)	Cu1–N1	1.999(8)
Mo2–O7	1.909(6)	Cu1–N2	1.996(7)
Mo2–O8	1.675(5)	Cu1–N3	1.973(7)
Mo2–O9	1.694(6)	V1–O1	1.660(6)
Mo2–O10	1.926(5)	V1–O2	1.755(6)
Mo2–O4[1]	2.368(5)	V1–O3	1.726(5)
Mo3–O2	2.331(5)	V1–O4	1.741(6)
Mo3–O10	1.906(5)		
angle	°	angle	°
O3–Mo1–O5	163.3(3)	O4[1]–Mo2–O9	90.8(3)
O3–Mo1–O6	91.9(3)	O4[1]–Mo2–O10	74.0(2)
O3–Mo1–O7	74.9(2)	O2–Mo3–O10	81.6(2)
O2[1]–Mo1–O3	74.66(18)	O2–Mo3–O11	164.3(2)
O3–Mo1–O12[1]	80.4(2)	O2–Mo3–O12	74.5(2)
O5–Mo1–O6	104.4(3)	O2–Mo3–O13	89.2(2)
O5–Mo1–O7	98.0(3)	O2–Mo3–O4[1]	76.32(18)
O2[1]–Mo1–O5	89.5(3)	O10–Mo3–O11	100.7(2)
O5–Mo1–O12[1]	101.0(3)	O10–Mo3–O12	149.3(3)
O6–Mo1–O7	100.6(3)	O10–Mo3–O13	97.9(2)
O2[1]–Mo1–O6	165.2(2)	O4[1]–Mo3–O10	75.1(2)
O6–Mo1–O12[1]	97.2(3)	O11–Mo3–O12	97.5(2)
O2[1]–Mo1–O7	82.1(2)	O11–Mo3–O13	105.7(3)
O7–Mo1–O12[1]	149.9(2)	O4[1]–Mo3–O11	89.2(2)
O2[1]–Mo1–O12[1]	74.94(19)	O12–Mo3–O13	100.8(2)
O3–Mo2–O7	74.1(2)	O4[1]–Mo3–O12	80.6(2)
O3–Mo2–O8	90.3(2)	O4[1]–Mo3–O13	164.6(2)
O3–Mo2–O9	164.1(3)	O1–Cu1–O1S	87.1(2)
O3–Mo2–O10	81.4(2)	O1–Cu1–N1	95.2(3)
O3–Mo2–O4[1]	74.19(17)	O1–Cu1–N2	175.8(3)
O7–Mo2–O8	101.3(2)	O1–Cu1–N3	93.7(3)
O7–Mo2–O9	98.6(3)	O1S–Cu1–N1	94.1(3)
O7–Mo2–O10	148.8(2)	O1S–Cu1–N2	97.0(3)
O4[1]–Mo2–O7	80.9(2)	O1S–Cu1–N3	104.1(3)
O8–Mo2–O9	105.2(3)	N1–Cu1–N2	85.9(3)
O8–Mo2–O10	97.8(2)	N1–Cu1–N3	160.2(3)
O4[1]–Mo2–O8	163.2(2)	N2–Cu1–N3	84.1(3)

O9–Mo2–O10	99.9(3)	O1–V1–O2	107.3(3)
O1–V1–O3	109.9(2)	O1–V1–O4	109.2(3)
O2–V1–O3	110.1(3)	O2–V1–O4	110.9(2)
O3–V1–O4	109.4(3)		

[1] 2-x,2-y,1-z

Compound **3**

Bond	distance, Å	Bond	distance, Å
Mo1–O4	2.329(2)	Mo3–O12	1.718(3)
Mo1–O5	1.905(3)	Mo3–O13	1.707(3)
Mo1–O6	1.710(3)	Mo3–O1[1]	2.275(2)
Mo1–O7	1.715(3)	Mo3–O5[1]	1.922(3)
Mo1–O8	1.911(3)	Cu1–O1S	1.966(4)
Mo1–O2[1]	2.296(3)	Cu1–O9	2.417(3)
Mo2–O4	2.323(3)	Cu1–N1	2.025(5)
Mo2–O8	1.924(2)	Cu1–N2	1.986(3)
Mo2–O9	1.710(3)	Cu1–N3	2.015(4)
Mo2–O10	1.713(3)	Cu1–O13[2]	2.889(3)
Mo2–O11	1.914(2)	V1–O1	1.766(3)
Mo2–O1[1]	2.282(3)	V1–O2	1.763(3)
Mo3–O2	2.297(3)	V1–O3	1.624(3)
Mo3–O11	1.923(3)	V1–O4	1.752(3)
angle	°	angle	°
O4–Mo1–O5	80.77(12)	O1–V1–O3	108.09(14)
O4–Mo1–O6	164.47(12)	O1–V1–O4	109.92(11)
O4–Mo1–O7	90.57(13)	O2–V1–O3	108.19(14)
O4–Mo1–O8	74.43(10)	O2–V1–O4	109.97(12)
O2[1]–Mo1–O4	76.12(9)	O3–V1–O4	108.18(14)
O5–Mo1–O6	100.65(14)	O1[1]–Mo2–O10	90.76(11)
O5–Mo1–O7	97.86(13)	O1[1]–Mo2–O11	75.22(10)
O5–Mo1–O8	148.90(12)	O2–Mo3–O11	82.38(10)
O2[1]–Mo1–O5	74.69(11)	O2–Mo3–O12	89.20(12)
O6–Mo1–O7	104.46(15)	O2–Mo3–O13	164.82(13)
O6–Mo1–O8	98.49(12)	O1[1]–Mo3–O2	76.60(9)
O2[1]–Mo1–O6	89.27(11)	O2–Mo3–O5[1]	74.36(11)
O7–Mo1–O8	100.81(13)	O11–Mo3–O12	97.93(14)
O2[1]–Mo1–O7	165.52(13)	O11–Mo3–O13	101.84(13)
O2[1]–Mo1–O8	81.31(10)	O1[1]–Mo3–O11	75.24(10)
O4–Mo2–O8	74.36(10)	O5[1]–Mo3–O11	150.79(12)
O4–Mo2–O9	89.87(12)	O12–Mo3–O13	104.48(16)
O4–Mo2–O10	164.81(12)	O1[1]–Mo3–O12	164.85(13)
O4–Mo2–O11	82.31(10)	O5[1]–Mo3–O12	99.14(15)
O1[1]–Mo2–O4	75.46(10)	O1[1]–Mo3–O13	90.27(13)
O8–Mo2–O9	100.04(14)	O5[1]–Mo3–O13	96.61(12)
O8–Mo2–O10	97.48(14)	O1[1]–Mo3–O5[1]	82.29(12)
O8–Mo2–O11	150.01(11)	O1S–Cu1–O9	91.29(13)
O1[1]–Mo2–O8	80.80(10)	O1S–Cu1–N1	96.07(18)
O9–Mo2–O10	104.33(13)	O1S–Cu1–N2	177.52(15)
O9–Mo2–O11	98.46(14)	O1S–Cu1–N3	94.17(17)

O1[1]–Mo2–O9	164.58(12)	O1S–Cu1–O13[2]	92.40(13)
O10–Mo2–O11	100.56(14)	O9–Cu1–N1	85.23(15)
O13[2]–Cu1–N1	88.63(15)	O9–Cu1–N2	91.09(13)
N2–Cu1–N3	84.46(15)	O9–Cu1–N3	106.40(13)
O13[2]–Cu1–N2	85.32(12)	O9–Cu1–O13[2]	173.15(10)
O13[2]–Cu1–N3	79.09(12)	N1–Cu1–N2	84.86(16)
O1–V1–O2	112.37(12)	N1–Cu1–N3	164.32(17)

[1] 1-x,1-y,1-z; [2] x,-1+y,z

Table S2. Parameters of intra– and intermolecular hydrogen bonds for crystals structures of 1–3.

Complex 1

D-H	A	D-H	H..A	D..A	∠(D–H…A)	Symmetry code
N3–H3AA	O4	0.8900	2.3800	3.152(6)	146.00	1-x,1-y,1-z
N3–H3AA	O12	0.8900	2.2800	2.787(5)	116.00	-x,1-y,1-z
N1–H1A	O14	0.8900	2.0400	2.898(6)	162.00	
N1–H1B	O6	0.8900	2.2000	3.001(6)	149.00	1-x,-y,1-z
N3–H3AB	O2	0.8900	2.5000	3.017(5)	118.00	
N3–H3AB	O6	0.8900	2.0100	2.812(6)	148.00	
N2–H2A	O9	0.8900	2.3200	3.191(5)	166.00	1-x,-y,1-z
N2–H2B	O2	0.8900	2.2900	3.162(6)	168.00	1-x,1-y,1-z
N3–H3AC	O15A	0.8900	1.9800	2.87(2)	172.00	-x,1-y,1-z
N4–H4A	O12	0.8500	2.1000	2.904(5)	158.00	1-x,1-y,2-z
N4–H4B	O14	0.8500	1.9900	2.753(6)	149.00	
N4–H4C	O7	0.8500	2.3100	3.104(5)	156.00	
N4–H4C	O13	0.8500	2.5700	3.034(6)	115.00	1-x,1-y,2-z
N4–H4D	O11	0.8500	2.1400	2.938(6)	157.00	1+x,y,z
N4–H4D	O12	0.8500	2.4400	2.970(6)	122.00	1+x,y,z
O14–H14A	O9	0.8500	1.9500	2.733(7)	153.00	
O14–H14B	O3	0.8500	2.4200	3.066(6)	134.00	x,-1+y,z
O14–H14B	O10	0.8500	2.2800	2.847(6)	125.00	1-x,-y,2-z
O15A–H15C	O1	0.8500	2.0600	2.89(3)	164.00	
O15A–H15D	O10	0.8500	2.3300	3.17(2)	173.00	x,1+y,z
C1–H1D	O10	0.9700	2.4300	3.331(7)	155.00	1+x,y,z
C3B–H3BA	O5	0.9700	2.4600	3.397(11)	163.00	-x,1-y,1-z
C3B–H3BA	O12	0.9700	2.5100	3.059(9)	116.00	-x,1-y,1-z
C3B–H3BB	O2	0.9700	2.5100	3.116(12)	121.00	

Complex 2

D-H	A	D-H	H..A	D..A	∠(D–H…A)	Symmetry code
O1S–H1SA	O5	0.8800	2.0000	2.862(9)	165.00	2.5-x,y,z-0.5
N1–H1A	O3	0.8900	2.2800	3.011(9)	140.00	
N1–H1B	O7S	0.8900	2.0400	2.91(2)	164.00	
N1–H1B	O6S	0.8900	2.4900	3.32(6)	155.00	
N2–H2	O9S	0.9800	2.2600	3.230(10)	172.00	x,1.5-y,z-0.5
N2–H2	O8S	0.9800	2.3100	3.256(15)	162.00	x,1.5-y,z-0.5

O1S–H1SB	O0AA	0.8400	2.5000	3.33(2)	166.00	
N3S–H3SA	O2	0.8500	2.1300	2.962(9)	165.00	
N3S–H3SA	O13	0.8500	2.4600	2.952(8)	117.00	
N3–H3A	O9	0.8900	2.4500	3.110(9)	131.00	1.5-x,y,-1/2+z
N3–H3A	O11	0.8900	2.4400	3.158(9)	139.00	1.5-x,y,-1/2+z
N3–H3B	O13	0.8900	2.1500	2.935(9)	147.00	-1/2+x,2-y,1/2-z
N3S–H3SB	O9	0.8500	2.3600	2.950(10)	126.00	1.5-x,y,-1/2+z
N3S–H3SB	O11	0.8500	2.3100	2.939(9)	131.00	1.5-x,y,-1/2+z
N3S–H3SC	O4S	0.8500	1.9600	2.810(13)	175.00	
N3S–H3SD	O1S	0.8500	2.3900	3.237(10)	176.00	1/2+x,2-y,1/2-z
O4S–H4SA	O7	0.8500	2.0400	2.816(12)	151.00	1.5-x,y,-1/2+z
O7S–H7SA	O4S	0.8600	2.2700	2.91(2)	132.00	
O7S–H7SB	O10	0.8700	2.0200	2.818(19)	152.00	
C1–H1C	O7S	0.9700	2.4900	3.30(2)	141.00	3/2-x,3/2-y,z
C3–H3D	O6	0.9700	2.5400	3.451(12)	157.00	x,1.5-y,-1/2+z

Complex 3

D-H	A	D-H	H..A	D..A	∠(D–H…A)	Symmetry code
O1S–H1SA	O5	0.8500	2.1000	2.941(5)	169.00	1-x,-y,1-z
N1–H1A	O11	0.8900	2.4000	3.246(5)	159.00	
N1–H1B	O4S	0.8900	2.2200	3.079(7)	162.00	
N2–H2	O3S	0.9800	2.1000	2.971(5)	148.00	
O1S–H1SB	O7	0.8500	2.5900	3.255(6)	136.00	
O1S–H1SB	O3	0.8500	2.4400	3.125(5)	138.00	1-x,-y,1-z
N1S–H1SC	O3S	0.8500	2.2500	3.001(6)	148.00	1/2+x,1/2-y,1/2+z
N3–H3A	O10	0.8900	2.5600	3.218(5)	132.00	x,-1+y,z
N3–H3A	O1	0.8900	2.3100	3.146(5)	156.00	1-x,-y,1-z
N3–H3B	O2S	0.8900	2.4800	3.273(5)	149.00	
N1S–H1SD	O6	0.8500	2.1300	2.969(6)	171.00	1+x,y,z
N1S–H1SE	O5S	0.8500	1.9400	2.780(7)	169.00	
N1S–H1SF	O2	0.8500	2.2000	2.965(5)	149.00	
N1S–H1SF	O12	0.8500	2.4200	3.078(6)	134.00	
O4S–H4SA	O12	0.9100	2.3800	3.143(6)	142.00	x,-1+y,z
O4S–H4SB	O2S	0.8700	1.9500	2.810(6)	169.00	1+x,y,z
O2S–H2SA	O7	0.8500	1.9500	2.756(5)	159.00	
O2S–H2SB	O10	0.8500	1.9600	2.803(4)	175.00	1/2-x,-1/2+y,1/2-z
O3S–H3SA	O8	0.8500	2.0400	2.869(4)	167.00	1/2-x,-1/2+y,1/2-z
O3S–H3SB	O2S	0.8500	2.0200	2.818(5)	155.00	1/2-x,1/2+y,1/2-z
O5S–H5SA	O7	0.8500	2.4000	3.238(7)	171.00	1-x,-y,1-z
O5S–H5SB	O4S	0.8500	1.9800	2.822(8)	172.00	
C2–H2A	O12	0.98(7)	2.51(6)	3.465(7)	166(4)	3/2-x,-1/2+y,1/2-z

Table S3. Details of the TG/DTA analysis for 1–3.

#	T, °C	Weight loss per each stage, %		Assumed decomposition stages	DTA peak, °C	Assumed solid residue
		Obs.	Calc.			
1	70–450	22.86	22.28	–6H_2O, 2NH_3, 3en	108 endo, 202 endo, 224 endo, 320 exo, 406 exo, 600 endo	$CuO·V_2O_5·6MoO_3$ 77.14% (obs.), 77.72% (calc.)
2	30–450	25.90	24.20	–8H_2O, 2NH_3, 2dien	75 endo, 234 endo, 280 exo, 387 exo, 436 exo, 600 endo	$2CuO·V_2O_5·6MoO_3$ 74.10% (obs.), 75.80% (calc.)
3	50–450	26.69	26.69	–11H_2O, 2NH_3, 2dien	111 endo, 231 endo, 280 exo, 427 exo, 600 endo	$2CuO·V_2O_5·6MoO_3$ 73.31% (obs.), 73.31% (calc.)