SUPPLEMENTARY INFORMATION

Synthesis, structures and applications of electron-rich polyoxometalates

Nadiia I. Gumerova[a,b] and Annette Rompel[a*]

[a] Universität Wien, Fakultät für Chemie, Institut für Biophysikalische Chemie, Althanstr. 14, 1090 Wien, Austria. www.bpc. univie.ac.at

[b] On leave from: Department of Inorganic Chemistry, Donetsk National University, 21021 Vinnytsia, Ukraine

[*] Correspondence to: E-Mail: annette.rompel@univie.ac.at

Table S1 Selected details of synthesis and characterisation of reduced isopolyanions. The compounds in each section are presented in the ascending order of reduction degree.

Archetype	Formula	No. of accepted e^-	Educts	Synthesis condition	Characterized *by*	Application	Ref.
Isopolymolybdates							
Lindqvist	$[NBu_4]_3[Mo^{V}Mo^{VI}_5O_{19}]$	1	$[NBu_4]_2[Mo^{VI}_6O_{19}]$	electrolysis in DMF with NBu_4BF_4, at -1.1 V	EA, IR, EPR, polarography	nr	[1-3]
Hepta-molybdate	$[NH_3{}^{i}Pr]_6[Mo^{V}O_5(OH)Mo^{VI}_6O_{18}]$	1	$[NH_3{}^{i}Pr]_6[Mo^{VI}_7O_{24}]$	UV-irradiation of a single crystal $[NH_3Pr]_6[Mo^{VI}_7O_{24}]$ ($\lambda \geq 313$ nm)	EPR, single-crystal XRD	nr	[4,5]
χ-Octa	$(Bu_4N)_6[Mo^{VI}_6O_{17}(NC_6H_{11})_2][Mo^{V}_4Mo^{VI}_4O_{24}]$	4	α-$[NBu_4]_4[Mo^{VI}_8O_{26}]$, TETA, DCC	reflux in dry acetonitrile	EA, IR, ESI-MS, UV/Vis, CV, single-crystal XRD	nr	[6]
Keggin derivative	$[Me_3NH]_6[H_2Mo^{V}_{12}O_{28}(OH)_{12}(Mo^{VI}O_3)_4]$	12	$[NH_3{}^{i}Pr]_6[Mo^{VI}_7O_{24}]$	prolonged photolysis in aqueous solution, pH 5–6, 4 d	EA, IR, ESI-MS, CV, ^{95}Mo NMR, single-crystal XRD	anti-tumor activity[7], [8]	[9]
	$[Me_2NH_2]_6[H_2Mo^{V}_{12}O_{28}(OH)_{12}(Mo^{VI}O_3)_4]$	12	MoO_3, Na_2MoO_4, $C(CH_2OH)_4$, $(Et_4N)Cl$, Me_3NH, H_2O	HT 160 °C, 3 d	EA, IR, single-crystal XRD	nr	[10]
	$[H_4Mo^{IV}_6Mo^{VI}_7O_{36}py_6]\cdot H_2py_3\cdot 2H_2O$	12	$[Mo^{IV}_3O_4(H_2O)_9]^{4+}$, H_3nta, pyridine	HT 120 °C, 3 d, pH = 3	EA, IR, single-crystal XRD	nr	[11]
"Shrink-Wrapping"	$(C_6H_{13}N_4)_{10}[H_2Mo^{V}_4Mo^{VI}_{12}O_{52}]\cdot 34H_2O$	4	Na_2MoO_4, $Na_2S_2O_4$, HCl, HMTAH	pH 4–4.5	EA, IR, UV/Vis, single-crystal XRD, BVS, DFT, magnetometry	nr	[12]
Deca-molybdate	$(^{n}Bu_4N)[Mo^{V}_2Mo^{VI}_7O_{25}(OMe)_6(Mo^{II}NO)]$	2	(n-$Bu_4N)_2[Mo^{VI}_5O_{13}(OMe)_4(NO)$ {Na-(MeOH)}], VCl_3	reflux in methanol, 4 h	EA, IR, single-crystal XRD, electrochemistry, magnetometry, Hückel calc.	nr	[13]
	$(^{n}Bu_4N)_2[Mo^{V}_4Mo^{VI}_5O_{24}(OMe)_7(Mo^{II}NO)]$	4	(n-$Bu_4N)_2[Mo^{VI}_6O_{18}(NO)]$, $N_2H_4\cdot 2HCl$	reflux in 1:1 mixture of methanol and acetonitrile, 7 h	EA, IR, single-crystal XRD, electrochemistry, magnetometry, Hückel calc.	nr	[14]
Isopolytungstates							
Lindqvist	$[(C_2H_5)_4N][W^{V}W^{VI}_5O_{19}]\cdot 0.5H_2O$	1	Na_2WO_4, MoO_3, Mo, $Et_4NCl\cdot H_2O$, H_2O	HT 160 °C, 3,5 d	EA, IR, TGA, single-crystal XRD, magnetometry	nr	[14]
	$[H_3N(CH_2)_2NH_3]_2[W^{V}W^{VI}_5O_{19}]\cdot[H_2N(CH_2)_2NH_2]Cl\cdot 8H_2O$	1	Na_2WO_4, V, $H_2N(CH_2)_2NH_2\cdot 2HCl$, H_2O	HT 160 °C, 3,75 d	EA, IR, TGA, single-crystal XRD, magnetometry	nr	[14]

	$(CpFe^{+}Cp)_3[W^{V}W^{VI}_5O_{19}]$	1	Na_2WO_4, CH_3COONa, CH_3COOH, ferrocene, THF, HCl·	85 °C, 1 d	EA, IR, single-crystal XRD, magnetometry	nr	[15]
Meta-tungstate	$[H_2W^{V}_nW^{VI}_{10}O_{40}]^{(6+n)-}$ (n = 1, 2)	1 – 2	$Na_6[H_2W^{VI}_{12}O_{40}]$	electrolysis on a Hg cathode	EA, IR, UV/Vis, potentiometry, polarography, EPR	nr	[16, 17]
	$Rb_4H_8[H_2W^{IV}_3W^{IV}_9O_{40}]\cdot 18H_2O$	6	$Na_6[H_2W^{VI}_{12}O_{40}]$, RbCl, CH_3COONa	electrolysis on a Hg cathode at –0.53 V vs. SCE in 0.5 M HCl	EA, single-crystal XRD	nr	[18]
	$[NH_4]_4H_8[H_2W^{IV}_3W^{IV}_9O_{40}]$	6	$[NH_4]_6[H_2W^{VI}_{12}O_{40}]$	electrolysis on a Hg cathode at –0.41 V vs. Ag–AgCl (3.5 M KCl) in 0.5 M HCl	EA, IR, UV/Vis, CV, ^{183}W NMR	nr	[19]
	$[NH_4]_4H_8[H_2W^{IV}_3W^{IV}_9O_{40}]$	6	$[NH_4]_6[H_2W^{VI}_{12}O_{40}]$	electrolysis at 4.0 V vs. a graphite rod electrode in 2 M Na_2CO_3	EA, IR, powder XRD	electrocatalyst for hydrogen oxidation for fuel cell applications	[20]
	$[H_kW^{IV}_nW^{VI}_{12-n}O_{40}]^{(6+2n)-}$ (*n* = 3, 6, 9, 12)	6 – 24	$Na_6[H_2W^{VI}_{12}O_{40}]$	electrolysis on a Hg cathode		nr	[21, 22, 23]
Deca-tungstate	$[H_5O_2][NH_2{}^{i}Pr_2]_4[W^{V}W^{VI}_9O_{32}]\cdot 4H_2O$ + $[H_5O_2]_2[NH_2{}^{i}Pr_2]_4[W^{V}_2W^{VI}_8O_{32}]\cdot 4H_2O$	1 – 2	$[NH_2{}^{i}Pr_2]_4[W^{VI}_{10}O_{32}]$	UV photolysis (λ > 310 nm)	EA, IR, ^{183}W NMR, EPR, single-crystal XRD	nr	[24]
	$[C_6H_{16}N_4][HW^{V}W^{VI}_9O_{32}]$ + $[C_6H_{16}N_4][H_2W^{V}_2W^{VI}_8O_{32}]$	1 – 2	$[C_6H_{16}N_4][W^{VI}_{10}O_{32}]\cdot 2CH_3CN$	UV photolysis (λ > 300 nm), 20 h	EA, single-crystal XRD	nr	[25]
	$Na_4[HW^{V}W^{VI}_9O_{32}]$ + 4 $Na_4[H_2W^{V}_2W^{VI}_8O_{32}]$	1 – 2	Na_2WO_4, $HClO_4$, CH_3CN	1) 80 °C, pH = 1; 2) UV photolysis (λ > 300 nm), 20 h	EA, single-crystal XRD	nr	[25]
	$[NBu_4]_5[W^{V}W^{VI}_9O_{32}]$	1	$[NBu_4]_4[W^{VI}_{10}O_{32}]$	electrolysis in DMF at –1.3 V or UV photolysis	EA, IR, UV/Vis, EPR	nr	[26]
	$[NBu_4]_6[W^{V}_2W^{VI}_9O_{32}]$	2	$[NBu_4]_4[W^{VI}_{10}O_{32}]$	electrolysis in acetonitrile at –2.2 V	UV/Vis, ^{17}O and ^{183}W NMR, EPR	nr	[27]
Isopolyvanadates							
Lindqvist	cis-$(CN_3H_6)_2[V^{IV}V^{V}_5O_{13}((OCH_2)_3CCH_2OH)_2]\cdot 8H_2O$	1	cis-$Na_2[V^{IV}_6O_7(OH)_6((OCH_2)_3CCH_2OH)_2]\cdot 8H_2O$, H_2O_2	1) 40 °C, 1 h; 2) RT, 15 h	EA, IR, UV/Vis, CV, EPR, single-crystal XRD, magnetometry	nr	[28]
	$[V^{IV}_3V^{V}_3O_8(OCH_3)_{11}]$	3	1) $VO(O^{t}Bu)_3$, CH_3OH; 2) $VO(OCH_3)_3$, CH_3OH, $^{t}BuNOH$, I_2	HT 125 °C, 24 h	EA, IR, UV/Vis, CV, single-crystal XRD, BVS	nr	[29]
	$(TBA)_2[V^{IV}_3V^{V}_3O_{10}(OH)_3((OCH_2)_3CNO_2)_2]\cdot 0.67$	3	$(TBA)_2[V^{V}_6O_{10}(OH)_3((OCH_2)_3CNO$	RT, 5 h	EA, IR, single-crystal	inhibition	[31]

	CH_2Cl_2		$_2)_2]$, 1,1-methylphenylhydrazine, CH_2Cl_2		XRD	of the ATPase	
	$[V^{IV}_3V^{V}_2O_6(OCH_3)_{12}Fe^{III}OTf]$	3	$VO(OCH_3)_3$, $FeBr_2$, toluene, AgOTf, MeCN	85 °C, 110 h	EA, IR, ESI-MS, CV, single-crystal XRD, magnetometry	nr	32
	$[V^{IV}_4V^{V}_2O_7(OCH_3)_{12}]$	4	$VO(O^tBu)_3$, $N^nBu_4[BH_4]$, CH_3OH	HT 125 °C, 24 h	EA, IR, CV, single-crystal XRD, BVS	nr	33, 34
	$[V^{IV}_4V^{V}_2O_7(OC_2H_5)_{12}]$	4	$VO(OC_2H_5)_3$, $N^nBu_4[BH_4]$, C_2H_5OH	HT 125 °C, 24 h	EA, IR, CV, DCS, ESI-MS, single-crystal XRD, BVS	nr	35, 36
	$(^nBu_4N)_2[V^{IV}_4V^{V}_2O_9(OH)_4((OCH_2)_3CCH_3)_2]$	4	$(^nBu_4N)_2[V^{V}_6O_{13}((OCH_2)_3CCH_3)_2]$, 1-methyl-1-phenylhydrazine	RT, 5 h	EA, IR, UV/Vis, ^{17}O NMR, EPR, single-crystal XRD, electrochemistry, magnetometry	nr	37
	$(Me_3NH)[V^{IV}_5V^{IV}O_7\{(OCH_2)_3CCH_3\}]$	5	V_2O_3, V_2O_5, 1,1,1-tris(hydroxymethyl)ethane, Me_3NHCl, Et_3NHCl, H_2O	HT 210 °C, 17 h	EA, IR, single-crystal XRD, electrochemistry, magnetometry	nr	38
	$cis\text{-}Na_2[V^{IV}_6O_7(OH)_6((OCH_2)_3\ CCH_2OH)_2]\cdot 8H_2O$	6	$NaVO_3$, N_2H_5OH, pentaerythritol, H_2O	80 °C, 7 h	EA, IR, UV/Vis, CV, EPR, single-crystal XRD, magnetometry	nr	28
	$Ba[V^{IV}_6O_7(OH)_3((OCH_2)_3CCH_3)_3]\cdot 3H_2O$	6	V_2O_3, KVO_3, 1,1,1-tris(hydroxymethyl)ethane, $BaCl_2\cdot 2H_2O$, H_2O	HT 150 °C, 50 h	EA, IR, single-crystal XRD, electrochemistry, magnetometry	nr	38
	$Na_2[V^{IV}_6O_7\{(OCH_2)_3CCH_2CH_3\}_4]$	6	V_2O_3, $NaVO_3$, 1,1,1-tris(hydroxymethyl)propane, NaCl, H_2O	HT 150 °C, 21 h	EA, IR, single-crystal XRD, electrochemistry, magnetometry	nr	38
	$(^nBu_4N)_2[V^{IV}_6O_7(OH)_6((OCH_2)_3CCH_3)_2]$	6	$(^nBu_4N)_2[V^{V}_6O_{13}((OCH_2)_3CCH_3)_2]$, CH_2Cl_2, 1,2-diphenylhydrazine	RT, 10 h	EA, IR, UV/Vis, ^{17}O NMR, EPR, single-crystal XRD, electrochemistry, magnetometry	nr	37
	$(cat)[V^{III}V^{IV}_5O_6(OCH_3)_8(calix)(CH_3OH)]$ (cat = Et_4N, NH_4, PyH, Et_3NH)	6	$VOSO_4$, calix, CH_3OH and one of base (Et_4NOH, NH_4OH, Et_3N, pyridine)	HT 170 °C, 3 d	EA, IR, single-crystal XRD, magnetometry, DFT	nr	39
Deca-vanadate	$(NH_4)_4[V^{IV}_{10}O_{16}(CH_3CH_2C(CH_2O)_3)_4]\cdot 4H_2O$	10	V_2O_3, NH_4VO_3, 1,1,1-tris(hydroxymethyl)propane, NH_4Cl, H_2O	HT 150 °C, 20 h	EA, IR, single-crystal XRD, electrochemistry, magnetometry	nr	34
	$(Et_4N)[V^{IV}_{10}O_{13}(CH_3CH_2C(CH_2O)_3)_5]$	10	V_2O_3, V_2O_5, 1,1,1-	HT 200 °C, 22 h	EA, IR, single-crystal	nr	34

			tris(hydroxymethyl)propane, TMABr, TMACl, H_2O		XRD, electrochemistry, magnetometry		
	$(Me_3NH)_2[V^{IV}_{10}O_{14}(OH)_2((OCH_2)CCH_2OH)_4]\cdot 2H_2O$	10	V_2O_3, V_2O_5, $NaVO_3$, pentaerythritol, Et_3NHCl, H_2O	HT 150 °C, 20 h	EA, IR, CV, single-crystal XRD, magnetometry	nr	[40]
	$Na_2[V^{IV}_8V^{V}_2O_{16}((OCH_2)CCH_2CH_3)_4]$	8	V_2O_3, $NaVO_3$, NaCl, Cu_2Br, 1,1,1-tris(hydroxymethyl)propane, H_2O	HT 150 °C, 50 h	EA, IR, CV, single-crystal XRD, magnetometry	nr	[40]
	$K_2[V^{IV}_8V^{V}_2O_{16}((OCH_2)CCH_2CH_3)]\cdot 2H_2O$	8	V_2O_3, KVO_3, KCl, $MnCl_2$, 1,1,1-tris(hydroxymethyl)propane, H_2O	HT 150 °C, 40 h	EA, IR, CV, single-crystal XRD, magnetometry	nr	[40]
	$(Bu_4N)_2[V^{IV}_8V^{V}_2O_{16}((OCH_2)CCH_2CH_3)]$	8	V_2O_3, V_2O_5, $VOSO_4$, 1,1,1-tris(hydroxymethyl)ethane, Bu_4NOH, H_2O	HT 150 °C, 90 h	EA, IR, single-crystal XRD, magnetometry	nr	[40]
"Wheel-like" deca-vanadate	$(n\text{-}Bu_4N)_4[V^{IV}_2V^{V}_8O_{26}]\cdot H_2O$	2	$(n\text{-}Bu_4N)_2[\{(\eta_3\text{-}C_4H_7)Pd\}_2V_4O_{12}]$, CH_3CN	reflux under N_2, 2 h	EA, single-crystal XRD	nr	[41]
	$(Et_4N)_4[V^{IV}_2V^{V}_8O_{26}]\cdot H_2O$	2	$VO(acac)_2$, $Cu(acac)_2$, CH_2Cl_2, Et_4NCl	RT, 1h	EA, IR, EPR, TGA, single-crystal XRD	nr	[42, 43]
	$(^nBu_4N)_4[V^{IV}_2V^{V}_8O_{26}]\cdot 2$ DMF	2	$(^nBu_4N)_4[V^{V}_4O_{12}]$, DMF, N-*tert*-butyl diethanolamine	UV irradiation (λ > 380 nm), 90 °C, overnight	EA, IR, UV/Vis, single-crystal XRD	nr	[44, 45]
	$(^nBu_4N)_4[V^{IV}_2V^{V}_8O_{26}]$	2	V_2O_5, $VOSO_4$, $^nBu_4NOH$, acetone, H_2O	RT	EA, CV, EPR, magnetometry	nr	[46]

nr – not reported

Methods

BVS - bond valence sum calculation
CV – cyclic voltammetry
EA – elemental analysis
EPR – electron paramagnetic resonance
ESI-MS – eloctrospay ionization mass spectrometry
HT – hydrothermal synthesis
IR – infrared spectroscopy
NMR – nuclear magnetic resonance
PXRD – powder X-ray diffraction
RT – room temperature
Single-crystal XRD – single-crystal X-ray diffraction
TGA – thermogravimetric analysis
UV/Vis – ultraviolet-visible spectroscopy
XPS – X-ray photoelectron spectroscopy
SCE – saturated calomel electrode

Organic compounds

Bu – Butyl
Cp – ferrocene
DCC – N,N'-dicyclohexylcarbodiimide
Et – ethyl
HMTAH – hexamethylenetetramine
Me – Methyl
nta – nitrilotriacetate
^{i}Pr – Isopropyl
py - pyridine
TBA – Tetrabutylammonium
TETA – Triethylenetetramine
Tf – trifluormethansulfonat

Table S2 Selected details of synthesis and characterisation of reduced of no-capped Keggin type anions. The compounds in each section are presented in in the ascending order of reduction degree.

Hetero-ion X	Formula	No. of accepted e^-	Educts	Synthesis condition	Characterized *by*	Application	Ref.
POMos with Keggin anions $XMo^{V}_{n}Mo^{VI}_{12-n}$							
P^{V}	$[K_2Ag_{15}(L)_{10}(H_2O)_2][H(PMo^{V}Mo^{VI}_{11}O_{40})_2]$, L = 5-*o*-toloyl-*1H*-tetrazole	1	$H_3[PMo^{VI}_{12}O_{40}]$, $AgNO_3$, 5-*o*-tolyl-*1H*-tetrazole, HNO_3, H_2O	HT 160 °C, 3 d, pH = 2.13	EA, IR, UV/Vis, single-crystal XRD	photocatalyst for degradation of organic dyes	47
	$[Ni(H_2O)_6][H_3PMo^{V}Mo^{VI}_{11}O_{40}]_2{\cdot}30H_2O$	1	Na_2MoO_4, HCl, H_3PO_4, $N_2H_5(HSO_4)$, Ni^{2+}	RT	EA, IR, single-crystal XRD	nr	48
	$[Cu^{I}(pz)_{1.5}]_4[PMo^{V}Mo^{VI}_{11}O_{40}]{\cdot}pz{\cdot}2H_2O$	1	$H_3PMo^{VI}_{12}O_{40}$, $CuCl_2$, pz, H_2O, HCl	HT 160 °C, 4 d, pH = 3.5	EA, IR, TGA, single-crystal XRD	electrocatalyst for reduction of H_2O_2	49
	$[Cu^{I}_3(pz)_3Cl][Cu^{I}_2(pz)_3(H_2O)][PMo^{V}Mo^{VI}_{11}O_{40}]$	1	$H_3PMo^{VI}_{12}O_{40}$, $CuCl_2$, pz, H_2O, HCl	HT 160 °C, 4 d, pH = 2	EA, IR, TGA, single-crystal XRD	electrocatalyst for reduction of H_2O_2	49
	$[Ag_4(2\text{-btz})_4(HPMo^{V}_2Mo^{VI}_{10}O_{40})]$	2	$H_3[PMo^{VI}_{12}O_{40}]$, $AgNO_3$, 2-btz, HNO_3, H_2O	HT 160 °C, 4 d, pH = 1.2	EA, IR, UV/Vis, single-crystal XRD	photocatalyst for degradation of organic dyes	50
	$[\{Ni(phen)_2(H_2O)\}_2](H_3O)[PMo^{V}_2Mo^{VI}_{10}O_{40}]{\cdot}4H_2O$	2	$NaVO_3$, Na_2MoO_4, $Ni(CH_3COO)_2$, phen, H_2O, H_3PO_4	HT 160 °C, 5 d, pH = 4.5	EA, IR, UV/Vis, single-crystal XRD	nr	51
	$(^{n}Bu_4N)_3[PMo^{V}_2Mo^{VI}_{10}O_{40}\{Co(MeCN)_2\}]$	2	$(^{n}Bu_4N)_3[PMo^{VI}_{12}O_{40}]$, $CoCl_2$, CH_3CN, Na/Hg amalgam	12 h	EA, IR, ^{31}P NMR, CV, single-crystal XRD	nr	52
	$[Ni(phen)_3][PMo^{V}_3Mo^{VI}_9O_{40}\{Ni(phen)\}_2]$	3	$(NH_4)_6Mo^{VI}_7O_{24}$, $NiCl_2$, H_3PO_4, 1,10-phen, H_2O	HT 160 °C, 7 d, pH = 3.8	EA, IR, UV/Vis, EPR, single-crystal XRD	nr	53
	$Ca_{0.5}H_6PMo^{V}_4Mo^{VI}_8O_{40}{\cdot}18H_2O$	4	Na_2MoO_4, H_3PO_4, HCl, $CaCl_2{\cdot}2H_2O$	electrolysis under N_2 on a Pt electrode, at –0.2 V vs. SCE	EA, single-crystal XRD	nr	54
	$(C_9H_7NO)_4H_7[PMo^{V}_4Mo^{VI}_8O_{40}]{\cdot}3H_2O$	4	$H_7[PMo^{V}_4Mo^{VI}_8O_{40}]$, Quinolin-8-ol, MeCN,		EA, IR, ^{31}P NMR, single-crystal XRD	nr	55
	$[Co^{II}(bpy)_3]_6(H_2bpy)[(Co^{II}bpy)_2(PMo^{V}_4Mo^{VI}_8O_{40})]_3[(Co^{II}bpy)(PMo^{V}_4Mo^{VI}_8O_{40})]{\cdot}16H_2O$	4	Na_2MoO_4,$Co(Ac)_2$, 2,2'-bpy, 4,4'-bis(phosphonomethyl)biphenyl, Na_2HPO_4, H_3PO_4, H_2O	HT 220 °C, 3 d	EA, IR, ^{1}H NMR, CV, XPS, TGA, single-crystal XRD	water oxidation to generate O_2 under visible light irradiation	56
	$[TBA]_3[H_4PMo_8^{V}Mo_4^{VI}O_{40}Zn_4][C_7H_6(COO)_2]_2$	8	Na_2MoO_4, Mo, $ZnCl_2$, H_3PO_4, $H_2C_2O_4$, TBAOH, H_2O	HT 180 °C, 3 d, pH = 4.9	EA, IR, TGA, PXRD, single-crystal XRD	electrocatalyst for reduction of BrO_3^-	57, 58
	$[H_3O][Hdma]_3[H_2phen]\{[Cr(phen)]_2[Mo^{V}_9Mo^{VI}_3O_3{}_6(PO_4)]\}{\cdot}nH_2O(n \approx 1)$	9	$(NH_4)_2MoO_4$, $K_2Cr_2O_7$, H_3PO_3, phen, DMF, H_2O	HT 160 °C, 7 d	EA, IR, UV/Vis, XPS, TGA, cerate oxidimetry, single-crystal XRD	nr	59

S^{VI}	α-$[NBu_4]_3[S^{VI}Mo^{V}Mo^{VI}{}_{11}O_{40}]$	1	$[NHex_4]_2[SMo^{VI}{}_{12}O_{40}]$, CH_2Cl_2	electrolysis, at –0.1 V vs. Fc^+/Fc	EA, IR, EPR, single-crystal XRD, electrochemistry	nr	[60]
Ge^{IV}	$[GeMo^{V}{}_8Mo^{VI}{}_4O_{36}(\mu_2\text{-}OH)_4\{Ni(pda)(H_2O)\}_2\{Ni(pda)\}\{Ni(pda)(bpe)\}(bpe)_{0.5}]_n$	8	Na_2MoO_4, GeO_2, $Ni(CH_3COO)_2$, pda, bpe, H_2O, H_2SO_4	HT 170 °C, 4 d, pH = 6.0	EA, IR, XPS, TGA, single-crystal XRD, magnetometry	nr	[61]
Ni^{II}	$[Mo^{V}{}_8Mo^{VI}{}_4O_{30}(\mu_2\text{-}OH)_6(Ni^{II}O4)\{Ni^{II}(en)(H_2O)\}_4]$	8	MoO_3, $Ni(Ac)_2$, en, H_2O	HT 160 °C, 2 d	EA, single-crystal XRD	nr	[62]
	$[Mo^{V}{}_{12}O_{30}(\mu\text{-}OH)_{10}H_2\{Ni^{II}{}_4(H_2O)_{12}\}]$	12	$(NH_4)_6[Mo_7O_{24}]$, $Ni(OOCCH_3)_2$, $(N_2H_5)HSO_4$, CH_3COOH, H_2O	65 °C, 3 d	EA, IR, single-crystal XRD, magnetometry	nr	[63]
POTs with Keggin anions $XW^{V}{}_nW^{VI}{}_{12-n}$							
P^{V}	$NaCu^{I}{}_2(tib)_4(H_2O)_4[H_2PW^{V}W^{VI}{}_{11}O_{40}][H_2PW^{VI}{}_{12}O_{40}]\cdot 6H_2O$	1	Na_2WO_4, H_3PO_4, $Cu(NO_3)_2$, tib, C_2H_5OH, H_2O	HT 160 °C, 3 d, pH = 3.66	EA, IR, TGA, XPS, single-crystal XRD, electrochemistry	catalyst for epoxidation of olefins with H_2O_2	[64]
	$[Cu^{I}{}_4(bpmb)_4][PW^{V}W^{VI}{}_{11}O_{40}]$	1	$H_3PW^{VI}{}_{12}O_{40}$, $CuCl_2$, bpmb, HCl, H_2O	HT 160 °C, 4 d, pH = 3	EA, IR, powder XRD, single-crystal XRD, photoluminescence analysis	electrocatalyst for reduction of NO^{2-}, IO_3^- and oxidation of ascorbic acid	[65]
	$[Cu(2,2'\text{-}bpy)_2]_5[PW^{V}{}_2W^{VI}{}_{10}O_{40}]\cdot 2H_2O$	2	Na_2WO_4, NaH_2PO_4, $CuCl_2$, bpy, EtOH, H_2O	HT 160 °C, 6 d, pH = 5	EA, IR, single-crystal XRD, electrochemistry	electrocatalyst for reduction of NO^{2-}	[66]
	$Co(tib)_2[PW^{V}{}_3W^{VI}{}_9O_{38}]\cdot 5H_2O$	3	Na_2WO_4, H_3PO_4, $Co(NO_3)_2$, tib, H_2O	HT 160 °C, 3 d, pH = 4.35	EA, IR, TGA, XPS, single-crystal XRD, electrochemistry	nr	[64]
	$[Ni(enMe)_2(H_2O)_2]_2[Ni(enMe)_2PW^{V}{}_3W^{VI}{}_9O_{40}]\cdot H_2O$	3	Na_2WO_4, $NiCl_2$, enMe, H_2O, H_3PO_4	HT 180 °C, 3 d, pH = 5.0 – 5.5	EA, IR, XPS, single-crystal XRD	nr	[67]
	$NaH_6[PW^{V}{}_4W^{VI}{}_8O_{40}]\cdot 4H_2O$	4	$H_3PW^{VI}{}_{12}O_{40}$, HCl	electrolysis under N_2 at –0.7 V vs. SCE	EA, IR, UV/Vis, XPS, EPR, single-crystal XRD, electrochemistry	nr	[68]
	$[Na(H_2O)_2\{M^{I}(btp)_4\}(PW^{V}{}_4W^{VI}{}_8O_{39}]$ (M = Cu, Ag))	4	Na_2WO_4, $Cu(OAc)_2$ or $AgNO_3$, bpt, H_2O, H_3PO_4	HT 160 °C, 5 d, pH = 3.5	EA, IR, TGA, single-crystal XRD, electrochemistry	electrocatalyst for reduction of NO^{2-}; fluorescence properties at RT	[69]
Si^{IV}	$[Ag_4(2\text{-}btz)_5K(SiW^{V}W^{VI}{}_{11}O40)]\cdot 13H_2O$	1	$H_4[SiW^{VI}{}_{12}O_{40}]$, $AgNO_3$, 2-btz, HNO_3, H_2O	HT 160 °C, 4 d, pH = 1.5	EA, IR, UV/Vis, single-crystal XRD	nr	[50]
Al^{III}	$[Cu(2,2'\text{-}bipy)_2]\{AlW^{V}W^{VI}{}_{11}O_{40}[Cu(2,2'\text{-}bipy)_2]_2\}\cdot 2H_2O$	1	$Cu(CH_3COO)_2$, Na_2WO_4, 2,2'-bipyridine, EDTA, NaOH, Al_2O_3, H_2O	HT 180 °C, 3 d, pH = 5	EA, IR, EPR, TGA, single-crystal XRD	nr	[70]
	$Cs_6Na[AlW^{V}{}_2W^{VI}{}_{11}O_{40}]\cdot 14.5H_2O$	2	$Na_5[AlW^{VI}{}_{12}O_{40}]$, Cs^+	electrolysis under Ar at	EA, IR, CV, ^{27}Al NMR, single-crystal XRD	nr	[71]

				–0,13 V vs. NHE			
Co^{II}	$K_{7.77}[Co^{II}W^{V}_{2}W^{VI}_{10}O_{40}]_{0.885}[Co^{II}W^{VI}_{12}O_{40}]_{0.115}\cdot 9.7H_2O$	2	$K_6[Co^{II}W^{VI}_{12}O_{40}]$, H_2O	electrolysis under N_2 at –0.69 V vs. SCE, pH = 3	EA, IR, single-crystal XRD	nr	[72]
Mixed Mo/W POMs with Keggin anions $XMo^{V}_{n}W^{VI}_{12-n}$							
As^{V}	$\{[Co(dien)]_4[(As^{V}O_4)Mo^{V}_{8}W^{VI}_{4}O_{33}(\mu\text{–}OH)_3]\}\cdot 2H_2O$	8	WO_3, MoO_3, As_2O_3, $Co(NO_3)_2$,dien, H_2O	HT 175 °C, 3 d, pH = 7	EA, IR, single-crystal XRD, magnetometry	nr	[73]
Si^{IV}	$[Cu_3(BTC)_2(H_2O)_3]_4[SiW^{VI}_{11}Mo^{V}O_{40}](C_4H_{12}N)_5\cdot 30H_2O$	1	$K_{8-x}Na_xSiW^{VI}_{11}O_{39}$, $(N(C_4H_9)_4)_{0.5}Na_{1.5}[Mo^{V}_{2}O_4(H_2O)_2(ox)_2]$, $CuCl_2\cdot 2H_2O$, H_3BTC,	HT 180 °C, 3 d, pH = 4.8	EA, IR, single-crystal XRD, magnetometry, proton conductivity measurements	nr	[74]
	$H_2[\alpha\text{-}SiMo^{V}_{2}W^{VI}_{10}O_{40}][Cu(PDA)_2\cdot H_2O]_2$	2	$K_{8-x}Na_xSiW^{VI}_{11}O_{39}$, $(N(C_4H_9)_4)_{0.5}Na_{1.5}[Mo^{V}_{2}O_4(H_2O)_2(ox)_2]$, $CuCl_2\cdot 2H_2O$, PDA	90 °C	EA, IR, UV/Vis, EPR, TGA, single-crystal XRD, magnetometry	nr	[75]
Ge^{IV}	$H_2[\alpha\text{-}GeMo^{V}_{2}W^{VI}_{10}O_{40}][Cu(DMF)_3H_2O]_2\cdot 5H_2O$	2	$K_{8-x}Na_xSiW^{VI}_{11}O_{39}$, $(N(C_4H_9)_4)_{0.5}Na_{1.5}[Mo^{V}_{2}O_4(H_2O)_2(ox)_2]$, $CuCl_2\cdot 2H_2O$, DMF	72 °C, pH = 7	EA, IR, single-crystal XRD, magnetometry	nr	[76]

nr – not reported

Methods

CV – cyclic voltammetry
EA – elemental analysis
EPR – electron paramagnetic resonance
HT – hydrothermal synthesis
IR – infrared spectroscopy
NHE – normal hydrogen electrode
NMR – nuclear magnetic resonance
PXRD – powder X-ray diffraction
RT – room temperature
SCE – saturated calomel electrode
Single-crystal XRD – single-crystal X-ray diffraction
TGA – thermogravimetric analysis
UV/Vis – ultraviolet-visible spectroscopy
XPS – X-ray photoelectron spectroscopy

Organic compounds

Ac – acetate
bpe – 1,2-bis(4-pyridine)-ethane
bpmb – 1,4-bis(pyrazol-1-ylmethyl)benzene
bpy – bipyridine
btp – 1,3-bis(1,2,4-triazol-1-yl)propane
BTC – 1,3,5-benzenetricarboxylate
btz – 1-benzyl-1*H*-(1,2,4)triazole
Bu – butyl
dien – diethylenetriamine
dma – dimethylamine
DMF – dimethylforamid
EDTA – ethylenediaminetetraacetic acid
en – ethylenediamine
enMe – 1,2-diaminopropane
pda – propanediamide
phen – 1,10-phenanthroline
pz – pyrazine
tib – 1,3,5-tris(1-imida-zolyl)benzene
ox – oxalate

Table S3 Selected details of synthesis and characterisation of reduced bi-capped Keggin type anions. The compounds in each section are presented in in the ascending order of reduction degree.

Hetero-ion X	Formula	No. of accepted e^-	Educts	Synthesis condition	Characterized *by*	Application	Ref.
Bi-capped bivanadyl POMos							
P^V	$(^nBu_4N)_3[PMo^V_4Mo^{VI}_8O_{40}(V^{IV}O)_2]$	6	$(^nBu_4N)_3[PMo^{VI}_{12}O_{40}]$, CH_3CN, $[V^VOCl_3(dme)]$, Na/Hg amalgam	19 h	EA, IR, ^{31}P NMR, CV, single-crystal XRD	nr	52
	$[Cu^I_5(2,4'\text{-bipy})_6(OH)][PMo^{VI}_8V^V_3V^{IV}O_{40}(V^{IV}O)_2]\cdot 1.5H_2O$	6	$NH_4V^VO_3$, $H_3[PMo^{VI}_{12}O_{40}]$, $Cu(CH_3CO_2)_2$, 2,4'- bipy, H_2O	HT 160 °C, 13 d	EA, IR, XPS, single-crystal XRD	nr	77
	$[\{Co(2,2'\text{-bipy})_2(H_2O)\}_2][PMo^V_5Mo^{VI}_7O_{40}(V^{IV}O)_2]$	7	$NaVO_3$, Na_2MoO_4, $Co(NO_3)_2$, 2,2'-bipy, H_3PO_4	HT 160 °C, 5 d, pH = 4.5	EA, IR, UV/Vis, single-crystal XRD	nr	51
	$[Cu^I6(2,3'\text{-bipy})_6(2,3'\text{-bipy-}2'\text{-O})_2][V^{IV}_2Mo^V_5Mo^{VI}_7O_{38}(PO_4)]$	7	NH_4VO_3, $H_3[PMo^{VI}_{12}O_{40}]$, $Cu(C_2O_2)_2$, 2,3'- bipy, H_2O	HT 160 °C, 13 d	EA, IR, XPS, single-crystal XRD	nr	77
	$(Et_3NH)_5[PMo^V_6Mo^{VI}_6O_{40}(V^{IV}O)_2]$	8	Na_2MoO_4, $V^{IV}OSO_4$, H_3PO_4, Et_3NHCl, H_2O	HT 180 °C, 3 d	EA, IR, UV/Vis, single-crystal XRD	nr	78
	$[PMo^V_4Mo^{VI}_8O_{40}(V^{IV}O_2)\{Co(phen)_2\}_2](H_3O)_2[PMo^V_8Mo^{VI}_4O_{40}(V^{IV}O_2)\{Co(phen)_2(H_2O)\}_2]$	9	$NaVO_3$, Na_2MoO_4, $Co(NO_3)_2$, phen, H_3PO_4, H_2O	HT 160 °C, 5 d, pH = 4.5	EA, IR, TGA, single-crystal XRD, magnetometry	nr	79
Si^{IV}	$[Ni(phen)_2][SiMo^V_2Mo^{VI}_{10}O_{40}(V^{IV}O)_2]\cdot 2trea\cdot 2H_2O$	4	$H_4[SiMo^{VI}_{12}O_{40}]$, $Ni(NO_3)_2$, NH_4VO_3, phen, trea, H_2O	HT 160 °C, 5 d	EA, IR, XPS, TGA, single-crystal XRD, magnetometry	nr	80
	$\{[Co(phen)_2]_2[SiMo^V_4Mo^{VI}_8O_{40}(V^{IV}O)_2]\}\{[Co(phen)_2(H_2O)_2][SiMo^V_4Mo^{VI}_8O_{40}(V^{IV}O)_2]\}\cdot 3H_2O$	6	$H_4[SiMo^{VI}_{12}O_{40}]$, $Co(NO_3)_2$, NH_4VO_3, phen, trea, H_2O	HT 160 °C, 5 d	EA, IR, XPS, TGA, single-crystal XRD, magnetometry	nr	80
	$[Cu^I(phen)_2]_2\{[Cu^I(phen)]_2[SiMo^V_4Mo^{VI}_8O_{40}(V^{IV}O)_2]\}$	6	$H_4[SiMo^{VI}_{12}O_{40}]$, $Cu(NO_3)_2$, NH_4VO_3, phen, trea, H_2O	HT 160 °C, 6 d	EA, IR, XPS, CV, TGA, single-crystal XRD, magnetometry	nr	81
Ge^{IV}	$\{[Co(phen)_2]_2[GeMo^V_4Mo^{VI}_8O_{40}(V^{IV}O)_2]\}\{[Co(phen)_2(H_2O)_2][GeMo^V_4Mo^{VI}_8O_{40}(V^{IV}O)_2]\}\cdot 3H_2O$	6	$H_4[GeMo^{VI}_{12}O_{40}]$, $Co(NO_3)_2$, $NH_4V^VO_3$, phen, trea, H_2O	HT 160 °C, 5 d	EA, IR, XPS, TGA, single-crystal XRD, magnetometry	nr	80
	$\{[Zn(phen)_2]_2[GeMo^V4Mo^{VI}_8O_{40}(V^{IV}O)_2]\}\{[Zn(phen)_2(H_2O)]_2[GeMo^V4Mo^{VI}_8O_{40}(V^{IV}O)_2]\}\cdot 3H_2O$	6	$H_4[GeMo^{VI}_{12}O_{40}]$, $Zn(NO_3)_2$, NH_4VO_3, phen, trea, H_2O	HT 160 °C, 6 d	EA, IR, CV, XPS, TGA, single-crystal XRD, magnetometry	nr	81
As^V	$[M(2,2'\text{-bipy})_2(H_2O)]_2[AsMo^V_5Mo^{VI}_7O_{40}(VO)_2]\}$, M = Co, Zn	7	$Li_3[AsMo^{VI}_{12}O_{40}]$, $M(NO_3)_2$ (M = Co, Zn), $NH_4V^VO_3$, 2,2'-bpy, trea, H_2O	HT 160 °C, 6 d	EA, IR, XPS, TGA, single-crystal XRD	electrocatalytic reduction of NO_2^- to NH_3	82
	$\{As^VMo^{VI}_6Mo^V_6O_{40}(V^{IV}O)[V^{IV}O(H_2O)]\}\cdot[Cu(4,4'\text{-bipy})]_5\cdot H_2O$	8	$Li_3[AsMo^{VI}_{12}O_{40}]$, $Cu(NO_3)_2$, NH_4VO_3, 4,4'-bpy, trea, H_2O	HT 165 °C, 6 d	EA, IR, CV, XPS, TGA, single-crystal XRD, magnetometry	nr	83
V^{IV}	$(Et_4N)_4[V^{IV}Mo^V_2Mo^{VI}_{10}V^V_2O_{44}]$		Na_2MoO_4, V_2O_5, 1,2,4,5-	HT 180 °C,	EA, IR, single-crystal	nr	84

			benzenetetracarboxylic acid, Et_4NCl, H_2SO_4	3,7 d	XRD		
Bi-capped bivanadyl mixed-metal POMo/Vs							
	{[Co(L)$_4$][HPMo$^{VI}_8$V$^{V}_4$O$_{40}$(V^{IV}O)$_2$]}, L = 1-(imidazol-1-yl)-4-(1,2,4-triazol-1-ylmethyl)benzene	2	$H_3PMo^{VI}_{12}O_{40}$, NH_4VO_3, $Co(CH_3COO)_2$, L, H_2O	HT 160 °C, 3 d	EA, IR, XPS, TGA, powder XRD, single-crystal XRD	electrocatalyst for the reduction of IO_3^- and oxidation ascorbic acid	85
	CoH(bix)$_4$[PMo$^{VI}_8$V$^{V}_4$O$_{40}$(V^{IV}O)$_2$]	2	Na_2MoO_4, $NaVO_3$, H_3PO_4, $CoCl_2$, bix, H_2O, HCl	HT 160 °C, 5 d, pH = 4	EA, IR, UV/Vis, TGA, single-crystal XRD	photocatalyst for degradation of RhB	86
	[HMn^{II}(bix)$_4$][PMo$^{VI}_8$V$^{V}_4$O$_{40}$(V^{IV}O)$_2$]·2H$_2$O	3	Na_2MoO_4, $NaV^{V}O_3$, H_3PO_4, $Mn(OAc)_2$, bix, H_2O, HCl	HT 170 °C, 6 d, pH = 5.1	EA, IR, UV/Vis, TGA, single-crystal XRD	photocatalyst for degradation of RhB	87
	[M(bix)$_4$][PMo$^{VI}_9$V$^{V}_3$O$_4$0(V^{IV}O)$_2$]·2H$_2$O, M = Zn^{II}, Cu^{II}	3	Na_2MoO_4, $NaVO_3$, H_3PO_4, $M(OAc)_2$, bix, H_2O, HCl	HT 170 °C, 6 d, pH = 5.1	EA, IR, UV/Vis, TGA, single-crystal XRD	photocatalyst for degradation of RhB	87
P^{V}	[Co(bpy)$_3$]$_2$[PMo$^{VI}_8$V$^{V}_3$V^{IV}O$_{40}$(V^{IV}O)$_2$][{Co(bpy)$_2$(H$_2$O)}$_2${PMo$^{VI}_8$V$^{V}_3$V^{IV}O$_{40}$(V^{IV}O)$_2$}]·8H$_2$O	3	$H_6P_2Mo^{VI}_{18}O_{62}$, NH_4VO_3, $CoCl_2$, H_2O	HT 180 °C, 4 d,	EA, IR, XPS, single-crystal XRD	nr	88
	[PMo$^{VI}_8$V$^{IV}_4$V$^{V}_2$O$_{42}$][M(Phen)$_2$(H$_2$O)]$_2$[TEA]$_2$·H$_3$O·3H$_2$O (M = Co, Ni, Zn)	4	NH_4VO_3, H_3PO_4, $H_3PMo^{VI}_{12}O_{40}$, M^{2+}, TEA, Phen, H_2O	HT 160 °C, 3 d, pH = 6	EA, IR, UV/Vis, XPS, single-crystal XRD	nr	89
	[PMo$^{VI}_8$V$^{IV}_5$V$^{V}_1$O$_{42}$][Co(Phen)$_2$]$_2$[Hpy]·3H$_3$O·H$_2$O	5	$NH_4V^{V}O_3$, H_3PO_4, $H_3PMo^{VI}_{12}O_{40}$, $CoCl_2$, TEA, Phen, py, H_2O	HT 160 °C, 3 d, pH = 4	EA, IR, UV/Vis, XPS, single-crystal XRD	nr	89
	[{PMo$^{VI}_5$Mo$^{V}_3$V$^{V}_4$V$^{IV}_2$O$_{42}$}{Co^{II}(H$_2$O)(2,2'-bpy)$_2$}$_2$][Co^{II}(2,2'-bpy)$_3$]$_2${PMo$^{VI}_7$Mo^{V}V$^{V}_6$O$_{42}$}·6H$_2$O	5	Na_2MoO_4, NH_4VO_3, H_3PO_4, $Co(OAc)_2$, 2,2'-py, H_2O	HT 160 °C, 5 d,	EA, IR, TGA, single-crystal XRD	nr	90
	[{PMo$^{VI}_6$Mo$^{V}_2$V$^{V}_3$V$^{IV}_3$O$_{42}$}{Cu^{II}(2,2'-bpy)}{Cu^{II}(2,2'-bpy)$_2$}$_2$]·3.5H$_2$O	5	Na_2MoO_4, NH_4VO_3, H_3PO_4, $Cu(OAc)_2$, 2,2'-bpy, H_2O	HT 160 °C, 5 d	EA, IR, TGA, single-crystal XRD	nr	90
	[Co$_4$(phen)$_8$(H$_2$O)$_2$(HPO$_3$)$_2$](H$_3$O)$_3$[PMo$^{VI}_8$V$^{IV}_4$O$_{40}$(V^{IV}O)$_2$]	6	Na_2MoO_4, NH_4VO_3, H_3PO_4, $CoCl_2$, phen, H_2O	HT 160 °C, 6 d, pH = 4	EA, IR, UV/Vis, XPS, EPR, TGA, single-crystal XRD	nr	91
	[Cu^{I}(phen)$_2$]$_4$[PMo$^{VI}_8$V$^{IV}_6$O$_{42}${Cu^{I}(phen)}$_2$]·H$_5$O$_2$	6	Na_2MoO_4, $NH_4V^{V}O_3$, H_3PO_4, $CuCl_2$, phen, H_2O	HT 160 °C, 7 d, pH = 4,4	EA, IR, UV/Vis, EPR, TGA, single-crystal XRD	nr	53
V^{V}	[Ni(enMe)$_2$][(V^{V}Mo^{V}I$_8$V$^{IV}_4$O$_{40}$)(V^{IV}O)$_2$]$_2$}·10H$_2$O	6	Na_2MoO_4, $NaVO_3$, HCl, enMe, $NiCl_2$	HT 160 °C, 4 d, pH = 3,7	EA, IR, UV/Vis, single-crystal XRD	photocatalytic degradation of RhB	92
	$Na_{0.5}K_{6.5}$[Mo$^{VI}_8$V$^{IV}_4$O$_{36}$(V^{V}O$_4$)(V^{IV}O)$_2$]·12.5H2O	6	Na_2MoO_4, KCl, $VOCl_2$, H_2O	45 – 50°C (Ar atm.), 5 d, pH = 6,2	EA, IR, single-crystal XRD	nr	93
Bi-capped bivanadyl POTs and PONs							
V^{IV}	[NiL$_4$V^{IV}W$^{V}_2$W$^{VI}_{10}$O$_{40}$(V^{IV}O)$_2$], L = 1,4-bis(imidazol-1-ylmethyl)benzene	4	Na_2WO_4, V_2O_5, $NiCl_2$, L, H_2O	HT 160 °C, 5 d, pH = 6,5	EA, IR, TGA, single-crystal XRD	photocatalyst for photodegradatio	94

						n of dyes	
Ge^{IV}	$\{Cu(en)_2\}_6\{GeNb^{V}_{12}V^{IV}_{2}O_{42}\}\cdot 20H_2O$	2	$K_7HNb_6O_{19}$, $Cu(OAc)_2$, $NaVO_3$, GeO_2, NaOH	HT 160 °C, 3 d, pH = 12	EA, IR, TGA, single-crystal XRD	antitumor activity	[95]
As^{V}	$[Ni(enMe)_2]_4\{[Ni(enMe)_2][Ni(enMe)_2(H_2O)AsW^{V}_{4}W^{VI}_{6}V^{IV}_{4}O_{42}\}\cdot 6H_2O$	8	Na_3AsO_4, Na_2WO_4, V_2O_5, $NiCl_2$, enMe, H_2O	HT 180 °C, 3 d, pH = 6.5–7	EA, IR, XPS, single-crystal XRD	nr	[67]
V^{V}	$[Cu(en)_2]_{3.5}[Cu(en)_2(H_2O)]\{[V^{V}Nb^{V}_{12}O_{40}(V^{IV}O)_2][Cu(en)_2]\}\cdot 17H_2O$	2	$K_7HNb_6O_{19}$, $NaVO_3$, $CuSO_4$, en	HT 110 °C, 4 d, pH = 12,3	EA, IR, single-crystal XRD	nr	[96]
Bi-capped with $Mo^{V/VI}$ or Sb^{III} ions POMos							
Si^{IV}	$(TMA)_5[SiMo^{V}_{4}Mo^{VI}_{10}O_{44}]$	4	$[Mo^{VI}_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6]$, Na_2SiO_3, HCl, TMAOH, H_2O	HT 150 °C, 36 h, pH = 4	EA, IR, single-crystal XRD, magnetometry	nr	97
	$(TMA)_6[Si_2Mo^{V}_{14}Mo^{VI}_{14}O_{84}(H_2O)]\cdot 2H_2O$	7	$[Mo^{VI}_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6]$, Na_2SiO_3, HCl, TMAOH, H_2O	HT 150 °C, 36 h, pH = 2	EA, IR, single-crystal XRD, magnetometry	nr	97
Al^{III}	$(H_2bpp)_{1/2}(H_2bpp)_2[AlMo^{V}_{4}Mo^{VI}_{8}O_{40}(Mo^{VI}O_2)_2]\cdot 2H_2O$	4	$AlCl_3$, Na_2MoO_4, $NiCl_2$, bpp, H_2O	HT 160 °C, 5 d, pH = 4.3	EA, IR, XPS, single-crystal XRD	catalytic oxidation of cyclohexanol to cyclohexanone	98
As^{V}	$(NH_4)[Mo^{VI}_{6}Mo^{V}_{6}O_{36}(As^{V}O_4)Mo^{V}(Mo^{V}O)]$	8	$(NH_4)_6Mo^{VI}_{7}O_{24}$, $NaAsO_2$, CH_3COONH_4, $N_2H_6SO_4$, $Mn(OAc)_2$, H_2O, HCl	HT 150 °C, 6 d, pH = 0.5	EA, IR, TGA, XPS, single-crystal XRD	H_2O_2-based oxidation of styrene	99
P^{V}	$(C_2N_2H_9)_2[PMo^{V}_{5}Mo^{VI}_{7}Sb^{III}_{2}O_{40}]\cdot 2H_2O$	5	$(NH_4)_6Mo^{VI}_{7}O_{24}$, Sb_2O_3, H_3PO_4, en, H_2O	HT 185 °C, 3 d, pH = 7	EA, IR, TGA, XPS, single-crystal XRD	nr	[100]
	$[PMo^{V}_{5}Mo^{VI}_{7}Sb^{III}_{2}O_{40}][M^{II}(enMe)_2]\cdot 4H_2O$, M = Cu, Ni	5	$(NH_4)_6Mo^{VI}_{7}O_{24}$, H_3PO_4, Sb_2O_3, M^{2+}, en, H_2O, HCl	HT 160 °C, 3 d,	EA, IR, TGA, XPS, single-crystal XRD	nr	[101]
	$(^{n}Bu4N)3[PMo^{V}_{6}Mo^{VI}_{6}Sb^{III}_{2}O_{40}]$	6	$(^{n}Bu_4N)_3[PMo^{VI}_{12}O_{40}]$, CH_3CN, $SbCl_3$, Na/Hg amalgam	30 h	EA, IR, ^{31}P NMR, CV, single-crystal XRD	nr	[52]

nr – not reported

Methods

CV – cyclic voltammetry
EA – elemental analysis
EPR – electron paramagnetic resonance
HT – hydrothermal synthesis
IR – infrared spectroscopy
NMR – nuclear magnetic resonance
PXRD – powder X-ray diffraction
RT – room temperature
SCE – saturated calomel electrode
Single-crystal XRD – single-crystal X-ray diffraction
TGA – thermogravimetric analysis
UV-vis – ultraviolet-visible spectroscopy
XPS – X-ray photoelectron spectroscopy

Organic compounds

Ac – acetate
bipy – bipyridine
bix – 1,4-bis(imidazol-1-ylmethyl)benzene
bpp – 1,3-di(4-pyridyl)propane
bpy – bipyridine
Bu – butyl
dme – 1,2-dimethoxyethane
en – ethylenediamine
enMe – 1,2-diaminopropane
Et – etyl
phen – 1,10-phenanthroline
py – pyridine
RhB – rhodamine B
TEA – triethylamine
TMA - tetramethylammonium
trea – triethylamine

Table S4 Selected details of synthesis and characterisation of reduced tetra-capped Keggin type anions. The compounds in each section are presented in in the ascending order of reduction degree.

Hetero ion X	Formula	No. of accepted e^-	Educts	Synthesis condition	Characterized *by*	Application	Ref.
			$\{XMo_8^{V/VI}V_8^{V/IV}\}$				
	$[Mo^{V}Mo^{VI}_{7}V^{IV}_{8}O_{40}(PO_4)][M(phen)_2(OH)]_2[M(phen)_2(OEt)]_2 \cdot xH_2O$ (M = Ni^{II}, Co^{II})	9	NH_4VO_3, H_2MoO_4, $(NH_4)_2HPO_4$, $M(NO_3)_2$, phen, 1,3-diaminopropane, H_2O, EtOH	HT 170 °C, 20 d	EA, IR, TGA single-crystal XRD, magnetometry	nr	[102]
	$[Ni(C_2N_2H_8)_3]_2Na[Mo^{V}_{2}Mo^{VI}_{6}V^{IV}_{8}O_{40}(PO_4)]\cdot H_2O$	10	NH_4VO_3, Na_2MoO_4, H_3PO_4, $Ni(OAc)_2$, en, H_2O	HT 160 °C, 6 d, pH = 6	EA, IR, TGA single-crystal XRD	nr	[103]
	$[PMo^{V}_{2}Mo^{VI}_{6}V^{IV}_{8}O_{44}\{Co(2,2'\text{-bipy})_2(H_2O)\}4]$-$[PMo^{VI}_{4}Mo^{V}_{4}V^{IV}_{8}O_{44}\{Co(2,2'\text{-bipy})_2(H_2O)\}_2]\cdot 4H_2O$	10	NH_4VO_3, Na_2MoO_4, $CoCl_2$, 2,2'-bipy, H_2O	HT 160 °C, 7 d, pH = 4,2	EA, IR, UV/Vis, EPR, single-crystal XRD	nr	[53]
	$\{[Ni(phen)_2(H2O)]_2[Ni(phen)_2][Mo^{V}_{2}Mo^{VI}_{6}V^{IV}_{8}O_{40}(PO_4)]\}$-$\{[Ni(phen)_2(H_2O)]_2[Mo^{V}_{2}Mo^{VI}_{6}V^{IV}_{8}O_{40}(PO_4)_2]\}\cdot 5H_2O\cdot 2EtOH$	10	NH_4VO_3, $H_3PMo^{VI}_{12}O_{40}$, $Ni(NO_3)_2$, phen, 1,3-diaminopropane, EtOH, H_2O	HT 170 °C, 6 d	EA, IR, EPR, XPS, single-crystal XRD, magnetometry	nr	[104]
	$\{Mo^{V}_{2}Mo^{VI}_{6}V^{IV}_{8}O_{40}(PO_4)[Co(phen)_2(H_2O)]_2\}[Co_2(phen)_2(OH)_2(H_2O)_4]_{1/2}$	10	NH_4VO_3, $H_3PMo^{VI}_{12}O_{40}$, $Co(en)_3Cl_3$, phen, H_2O	HT 170 °C, 6 d	EA, IR, single-crystal XRD	nr	[105]
	$[Co(en)_2][Co(bpy)_2]_2[PMo^{V}_{3}Mo^{VI}_{5}V^{IV}_{8}O_{44}]\cdot 4.5H_2O$	11	NH_4VO_3, $H_3PMo^{VI}_{12}O_{40}$, $Co(en)_3Cl_3$, 2,2'-bipy, H_2O	HT 170 °C, 6 d	EA, IR, XPS, TGA, single-crystal XRD	nr	[106]
P^V	$\{Mo^{V}_{3}Mo^{VI}_{5}V^{IV}_{8}O_{40}(PO_4)[Co(phen)(en)(H_2O)]_2\}[Co(phen)_3]\cdot 1.5H_2O$	11	NH_4VO_3, $H_3PMo^{VI}_{12}O_{40}$, Co(C2O4)2, en, phen, H_2O	HT 170 °C, 10 d	EA, IR, single-crystal XRD	nr	[105]
	$[Cu(en)_2]\{[Cu(en)_2]_2[Mo^{V}_{3}Mo^{VI}_{5}V^{IV}_{8}O_{40}(PO_4)]\}\cdot 4H_2O$	11	$(NH_4)_6Mo_7O_{24}$, NH_4VO_3, $VO(SO_4)$, H_3PO_3, $CuCl_2$, $H_2C_2O_4$, H_2O	HT 180 °C, 3 d, pH = 9	EA, IR, XPS, TGA, single-crystal XRD, magnetometry	nr	[107]
	$\{[M(2,2'\text{-bipy})_2H_2O]_4[Mo^{V}_{3}Mo^{VI}_{5}V^{IV}_{8}O_{40}(PO_4)]\}\{M(2,2'\text{-bipy})_2H_2O]_2[Mo^{V}_{3}Mo^{VI}_{5}V^{IV}_{8}O_{40}(PO_4)]\}\cdot xH_2O$ (M = Ni^{II}, Co^{II})	11	MCl_2, H_2MoO_4, V_2O_5, $H_2C_2O_4$, H_3PO_4, 2,2'-bipy, H_2O	HT 175 °C, 5 d,	EA, IR, EPR, XPS, single-crystal XRD, magnetometry	nr	[108]
	$\{[Mo^{V}_{3}Mo^{VI}_{5}V^{IV}_{8}O_{40}(PO_4)][Ni(en)_2]\}[Ni(en)_2]_2\cdot 4H_2O$	11	NH_4VO_3, $H_3PMo^{VI}_{12}O_{40}$, $Ni(NO_3)_2$, en, H_2O	HT 170 °C, 10 d	EA, IR, single-crystal XRD	nr	[109]
	$[Co(en)_2]\{[Co(en)_2]_2[HMo^{V}_{4}Mo^{VI}_{4}V^{IV}_{8}O_{40}(PO_4)]\}\cdot 5H_2O$	12	$(NH_4)_6Mo_7O_{24}$, NH_4VO_3, $VO(SO_4)$, H_3PO_3, $CoCl_2$, $H_2C_2O_4$, H_2O	HT 180 °C, 3 d, pH = 9	EA, IR, XPS, single-crystal XRD, magnetometry	nr	[107]
	$\{[Co(phen)_2]_2C_2O_4\}\{H_2PMo^{V}_{5}Mo^{VI}_{3}V^{IV}_{8}O_{44}[Co(phen)_2H_2O]_2\}\cdot 7H_2O$	13	NH_4VO_3, Na_2MoO_4, $CoCl_2$, $H_2C_2O_4$, H_3PO_4, phen, H_2O	HT 160 °C, 3 d, pH = 9	EA, IR, EPR, XPS, single-crystal XRD,	nr	[110]

					magnetometry		
	$[Ni(en)_2]\{[Ni(en)_2]_2[Mo^{V}_3Mo^{VI}_5V^{IV}_8O_{40}(V^{V}O_4)]\}\cdot 2H_2O$	11	$(NH_4)_6Mo_7O_{24}$, NH_4VO_3, $VO(SO_4)$, H_3PO_3, $Ni_2C_2O_4$, $H_2C_2O_4$, H_2O	HT 180 °C, 3 d, pH = 9	EA, IR, XPS, TGA, single-crystal XRD, magnetometry	nr	[107]
V^{V}	$[Ni(enMe)_2]_5\{[Ni(enMe)_2]_2[(V^{V}Mo^{V}_4Mo^{VI}_4V^{IV}_4O_{40})(V^{IV}O)_4]\cdot 2H_2O$	12	$NaVO_3$, Na_2MoO_4, $NiCl_2$, enMe, HCl, H_2O	HT 160 °C, 4 d, pH = 3.6	EA, IR, UV/Vis, single-crystal XRD	photocatalytic degradation of RhB	[92]
	$[\{(H_2O)Ni(enMe)_2Mo^{V}_4Mo^{VI}_4V^{IV}_8(V^{V}O_4)O_{40}\}_2\{Ni(enMe)_2\}][Ni(enMe)_2]_4\cdot 8H_2O$	12	V_2O_5, MoO_3, $NiCl_2$,enMe, H2O	HT 160 °C, 4 d	EA, IR, EPR, single-crystal XRD	nr	[111]
	$[Co_2(phen)_2(OH)_2(H_2O)_4]_{0.5}$-$[\{Co(phen)_2(H_2O)\}_2AsMo^{V}_2Mo^{VI}_6V^{IV}_8O_{44}]\cdot 2H2O$	10	NH_4VO_3, $H_3AsMo_{12}O_{40}$, $Co(en)_3Cl_3$, H_2O	HT 180 °C, 6 d	EA, IR, EPR, single-crystal XRD, magnetometry	nr	[112]
As^{V}	$[Ni(enMe)_2]_4\{[Ni(enMe)_2]$-$[Ni(enMe)_2(H_2O)AsMo^{V}_4Mo^{VI}_4V^{IV}_8O_{44}]_2\}\cdot 8H_2O$	12	Na_3AsO_4, $(NH_4)_6Mo_7O_{24}$, V_2O_5, $NiCl_2$, enMe, $H_2C_2O_4$, H_2O	HT 180 °C, 3 d, pH = 6.5–7	EA, IR, XPS, single-crystal XRD	nr	[67]

nr – not reported

Methods

CV – cyclic voltammetry
EA – elemental analysis
EPR – electron paramagnetic resonance
HT – hydrothermal synthesis
IR – infrared spectroscopy
NMR – nuclear magnetic resonance
PXRD – powder X-ray diffraction
RT – room temperature
Single-crystal XRD – single-crystal X-ray diffraction
SCE – saturated calomel electrode
TGA – thermogravimetric analysis
UV-vis – ultraviolet-visible spectroscopy
XPS – X-ray photoelectron spectroscopy

Organic compounds

Ac – acetate
bipy – bipyridine
bpy – bipyridine
en – ethylenediamine
enMe – 1,2-diaminopropane
Et – ethyl
EtOH – ethanol
phen – 1,10-phenanthroline
RhB – rhodamine B

Table S5 Selected details of synthesis and characterisation of reduced polyoxometalates with Dawson structure. The compounds in each section are presented in in the ascending order of reduction degree.

Hetero-ions X	Formula	No. of accepted e^-	Educts	Synthesis condition	Characterized *by*	Application	Ref.
			$\{X_2Mo_{18}O_{62}\}$				
SO_3^{2-}	$[TEAH]_6[Mo^{V}_2Mo^{VI}_{16}O_{54}(SO_3)_2]\cdot 4H_2O$	2	TEAH, Na_2Mo_4, $Na_2S_2O_4$, HCl, H_2O	pH = 4, 1 h	EA, IR, UV/Vis, single-crystal XRD, BVS, redox titration	nr	113
	$[^nBu_4N]_5[S_2Mo^{V}Mo^{VI}_{17}O_{62}]$	1	$[^nBu_4N]_4[S_2Mo^{VI}_{18}O_{62}]$, $^nBu_4NClO_4$	electrolysis at 400 mV vs. Ag–AgCl	EA, IR, EPR	nr	114
	$(C_{16}H_{18}N_3S)_5[S_2Mo^{V}Mo^{VI}_{17}O_{62}]\cdot CH_3CN$	1	$[^nBu_4N]_4[S_2Mo^{VI}_{18}O_{62}]$, CH_3CN, MB	RT	EA, IR, XPS, single-crystal XRD, magnetometry	reduction of NO_2^-, ClO_3^-, BrO_3^-, H_2O_2	115
SO_4^{2-}	$[Fe(\eta^5\text{-}C_5Me_5)_2]_5[HS_2Mo^{V}_2Mo^{VI}_{16}O_{62}]\cdot 3\ HCONMe_2\cdot 2\ Et_2O$	2	[Fe-(cp*)2], $[NHex_4]_4[S_2Mo_{18}O_{62}]$, MeCN	RT	EA, IR, ^1H NMR, EPR, CV, single-crystal XRD, magnetometry		116
	$[^nBu_4N]_6[S_2Mo^{V}_2Mo^{VI}_{16}O_{62}]$	2	$[^nBu_4N]_4[S_2Mo^{VI}_{18}O_{62}]$, $^nBu_4NClO_4$	electrolysis at 0 mV vs. Ag–AgCl	EA, IR, EPR	nr	114
	$[^nBu_4N]_5[H_3S_2Mo^{V}_4Mo^{VI}_{12}O_{62}]\cdot 4\ CH_3CN$	4	PPh_3, $[^nBu_4N]_4[S_2Mo^{VI}_{18}O_{62}]$, $CH_3CN\cdot$	reflux, 72 h	EA, IR, UV/Vis single-crystal XRD	nr	117
AsO_4^{3-}	$[Cu(2,2'\text{-bpy})_2][\{Cu(2,2'\text{-bpy})\}_3\{As^{V}_2Mo^{V}_2Mo^{VI}_{16}O_{62}\}]\cdot 4H_2O$	2	$(NH_4)_6Mo^{VI}_7O_{24}$, $NaAsO_2$, 2,2'-bpy, $CuCl_2$, HCl	HT 160 °C, 3 d, pH = 4	EA, IR, UV/Vis, XPS, PXRD, single-crystal XRD	electrocatalyst for the reduction of NO_2^-	118
	$[H_2(4,4'\text{-bpy})]_{2.5}[As^{III}(As^{V}_2Mo^{V}_2Mo^{VI}_{16}O_{62})]\cdot 5H_2O$	2	$(NH_4)_6Mo^{VI}_7O_{24}$, $NaAsO_2$, 4,4'-bpy, $CuCl_2$, HCl	HT 160 °C, 3 d, pH = 3	EA, IR, UV/Vis, XPS, PXRD, single-crystal XRD	electrocatalyst for the reduction of NO_2^-	118
	$(pyr)(imi)(Himi)_3[As^{III}_2(As^{V}_2Mo^{V}_3Mo^{VI}_{15}O_{62})]\cdot 3H_2O$	3	$(NH_4)_6Mo^{VI}_7O_{24}$, $NaAsO_2$, imi, $CuCl_2$, HCl	HT 160 °C, 3 d, pH = 2.5	EA, IR, UV/Vis, XPS, PXRD, single-crystal XRD	electrocatalyst for the reduction of NO_2^-	118
	$[As^{III}_3(As^{V}_2Mo^{V}_3Mo^{VI}_{15}O_{62})]\cdot 4H_2O$	3	$(NH_4)_6Mo^{VI}_7O_{24}$, $NaAsO_2$, imi, $CuCl_2$, HCl	HT 160 °C, 3 d, pH = 2	EA, IR, UV/Vis, XPS, PXRD, single-crystal XRD	electrocatalyst for the reduction of NO_2^-	118
			$\{X_2W_{18}O_{62}\}$				
SO_3^{2-}	$(Pr_4N)_5\{\alpha\text{-}[W^{V}W^{VI}_{17}O_{54}(SO_3)_2]\}\cdot 2\ CH_3CN$	1	$K_7Na[W^{VI}_{18}O_{56}(S^{IV}O_3)_2(H_2O)_2]\cdot 20H_2O$, $Na_2S_2O_4$, Pr_4NBr, HCl	RT, pH = 1	EA, IR, EPR, single-crystal XRD, electrochemistry, photochemistry	nr	119
ClO_4^-	$[^nBu_4N]_3[Cl_2W^{V}W^{VI}_{17}O_{62}]$	1	Na_2WO_4, DMF, HCl, $^nBu_4NBr$	UV irridation, HT 170 °C,	EA, IR, EPR, CV, single-crystal XRD	nr	120
AsO_4^{3-}	$[Cu_4(btb)_6(H_2O)_2][As_2W^{V}_2W^{VI}_{16}O_{62}]\cdot 10H_2O$	2	$\alpha\text{-}K_6As_2W^{VI}_{18}O_{62}$, Cu(NO3)2, btb, Et_3N		EA, IR, single-crystal	electrocatalyst for	121

				4 d, pH = 3.8	XRD, electrochemistry, photochemistry	the reduction of NO_2^-; photocatalytic degradation of MB	
			$\{X_2M_{18}O_{62}\}$				
	$[^nBu_4N]_7[P_2Mo^{V}Mo^{VI}{}_nW^{VI}{}_{17-n}O_{62}]$, n = 0, 1, 2	1	$[^nBu_4N]_7[P_2Mo^{VI}{}_nW^{VI}{}_{18-n}O_{62}]$ (n = 1 – 3), DMF	irridation by a Hg lamp	EA, IR, redox titration, ^{31}P NMR, magnetometry	nr	122
PO_4^{3-}	$K_8[V^{IV}OP_2Mo_2W_{15}O_{61}]\cdot16H_2O$	1	$K_{10}[P_2Mo_2W_{15}O_{61}]\cdot19H_2O$, CH_3COOH, LiOH, LiCl, $VOSO_4$, KCl		EA, IR, UV-Vis., ^{31}P NMR, CV	nr	123
	$K_9[H_4PV^{IV}W_{17}O_{62}]\cdot18H_2O$	1	$VOSO_4$, $K_{11}[H_4PW_{17}O_{61}]\cdot18H_2O$, HCl, KCl		EA, IR, UV-Vis., ^{31}P NMR, CV	oxidation of L-cysteine	124
AsO_3^{3-}	$K_8[V^{IV}OAs_2W_{17}O_{61}]\cdot16H_2O$	1	$[As_2W_{17}O_{61}]^{6-}$, $VOSO_4$		EA, IR, UV-Vis., ^{31}P NMR, CV	nr	125
SO_3^{2-}	$(NH_4)_7[Mo^{VI}{}_{11}V^{V}{}_5V^{IV}{}_2O_{52}(SO_3)]\cdot12H_2O$		$(NH_4)_6Mo^{VI}{}_7O_{24}\cdot4H_2O$, HCl, NH_4VO_3, $(NH_4)_2SO_3$	pH = 1,5	EA, IR, CSI-MS, EPR, single-crystal XRD	nr	126

nr – not reported

Methods

CSI-MS - cold-spray ionization mass spectrometry
CV – cyclic voltammetry
EA – elemental analysis
EPR – electron paramagnetic resonance
HT – hydrothermal synthesis
IR – infrared spectroscopy
NMR – nuclear magnetic resonance
PXRD – powder X-ray diffraction
RT – room temperature
Single-crystal XRD – single-crystal X-ray diffraction
UV-vis – ultraviolet-visible spectroscopy
XPS – X-ray photoelectron spectroscopy

Organic compounds

Bu – butyl
bpy – bipyridine
btb – 1,4-bis(1,2,4-triazol-1-y1)butane
DMF – dimethylforamid
$Fe(cp^*)_2$ – decamethylferrocene
imi – imidazol
MB – methylene blue
Me – methyl
Pr – isopropyl
PPh_3 – tiphenylphosphine
pyr – pyridine
TEAH – triethanolamine

Table S6 Selected details of synthesis and characterisation of reduced basket-like and borophosphate polyoxomolybdates. The compounds in each section are presented in in the ascending order of reduction degree.

M	Formula	No. of accepted e^-	Educts	Synthetis condition	Characterized *by*	Application	Ref.
			$\{M\subset P_6Mo^{V/VI}_{18}O_{73}\}$				
K^+	$[H_2dmpip]_5[K\subset P^V_6Mo^V_3Mo^{VI}_{15}O_{73}]$	3	MoO_3, Mo, dmpip, KH_2PO_4,H_3PO_4, H_2O	HT 150 °C, 5 d	EA, IR, UV/Vis, CV, single-crystal XRD	nr	127
	$[Cu_4(bpy)_4(H_2O)_4K\subset P_6Mo_{18}O_{71}(OH)_2]\cdot 7H_2O$	3	MoO_3, Mo, CuO, bpy, KH_2PO_4,H_3PO_4, H_2O	HT 150 °C, 5 d	EA, IR, single-crystal XRD, DFT calculation	nr	128
Ca^{2+}	$\{[Cu(2,2'\text{-bpy})(H_2O)]_4[Ca\subset P_6Mo^V_2Mo^{VI}_{16}O_{73}]\}\cdot 4H_2O$	2	Na_2MoO_4, $CuCl_2$, $CaCl_2$, H_3PO_4, NaOH, 2,2′-bpy, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV/Vis, XPS, single-crystal XRD	electrocatalytic reduction of NO_2^-	129
	$(H_2bih)_3[\{Cu^{II}(H_2O)_2\}\{Ca\subset P_6Mo^V_2Mo^{VI}_{16}O_{73}\}]\cdot 2H_2O$	2	$(NH_4)_6Mo^{VI}_7O_{24}$, $Cu(OAc)_2$, H_3PO_4, $CaCl_2$, bih, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV/Vis, XPS, single-crystal XRD	photocatalytic degradation of methyl orange, methylene blue, and RhB	130
	$(H_2bib)_3[\{Fe^{II}(H_2O)_2\}\{Ca\subset P_6Mo^V_2Mo^{VI}_{16}O_{73}\}]\cdot 4H_2O$	2	$(NH_4)_6Mo^{VI}_7O_{24}$, $Fe(Ac)_2$, H_3PO_4, $CaCl_2$, bib, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV/Vis, XPS, single-crystal XRD	photocatalytic degradation of methyl orange, methylene blue, and RhB	130
	$\{Cu(bim)_2\}\{[Cu(bim)_2]_2[Cu(Hbim)(H_2O)_2][Ca\subset P_6Mo^V_3Mo^{VI}_{15}O_{73}]\}\cdot 9H_2O$	3	Na_2MoO_4, $CuCl_2$, $CaCl_2$, H_3PO_4, NaOH, bim, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV/Vis, XPS, single-crystal XRD	electrocatalytic reduction of NO_2^-	129
	$[\{Cu^{II}(H_2O)_2\}\{Ca_4(H_2O)_4(HO_{0.5})_3(en)_2\}\{Ca\subset P_6Mo^V_4Mo^{VI}_{14}O_{73}\}]\cdot 7H_2O$	4	$(NH_4)_6Mo^{VI}_7O_{24}$, $Cu(OAc)_2$, H_3PO_4, $CaCl_2$, en, H_2O	HT 160 °C, 4 d, pH = 3	EA, IR, TGA, UV/Vis, XPS, single-crystal XRD	photocatalytic degradation of methyl orange, methylene blue, and RhB	130
Sr^{2+}	$\{H_2(4,4'\text{-bpy})\}_5\{[Ni(4,4'\text{-bpy})(H_2O)_3]_2[Ni(H_2O)_2][Sr\subset P_6Mo^V_2Mo^{VI}_{16}O_{73}]_2\}\cdot 12H_2O$	2	Na_2MoO_4, $NiCl_2$, $SrCl_2$, H_3PO_4, NaOH, 4,4′-bpy, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV/Vis, XPS, single-crystal XRD	electrocatalytic reduction of NO_2^-	129
	$(H_4bth)[\{Mn_2(H_2O)_3\}\{Sr\subset P_6Mo^V_2Mo^{VI}_{16}O_{73}\}]\cdot 3H_2O$	2	$(NH_4)_6Mo_7O_{24}$, $MnAc_2$, H_3PO_4, $SrCl_2$, bth, H_2O	HT 160 °C, 4 d, pH = 3	EA, IR, TGA, UV/Vis, XPS, PXRD, single-crystal XRD	photocatalytic degradation of MB, RhB, and AP; electrocatalytic reduction of NO_2^- and oxidation of ascorbic acid	131
	$(H_2L)[\{M^{II}(H_2O)_n\}_2\{Sr\subset P_6Mo^V_2Mo^{VI}_{16}O_{73}\}]\cdot xH_2O$ (L = bth, bih, bip; M = Fe, Co, Ni, Cu, Zn)	2	$(NH_4)_6Mo_7O_{24}$, M^{2+}, H_3PO_4, $SrCl_2$, L, H_2O	HT 160 °C, 4 d, pH = 3	EA, IR, TGA, UV/Vis, XPS, PXRD, single-crystal XRD	electrocatalytic reduction of H_2O_2 and oxidation of ascorbic asid	132

$(H_2bib)_3[\{M^{II}(H_2O)_2\}\{Sr \subset P_6Mo^{V}_2Mo^{VI}_{16}O_{73}\}]\cdot nH_2O$ (M = Fe, Co, Ni, Cu, Zn)	2	$(NH_4)_6Mo_7O_{24}$, M^{2+}, H_3PO_4, $SrCl_2$, bib, H_2O	HT 160 °C, 4 d, pH = 3	EA, IR, TGA, UV/Vis, XPS, PXRD, single-crystal XRD	photocatalytic degradation of MB, MO, and RhB; electrocatalytic reduction of NO_2^- and oxidation of ascorbic acid	133
$\{Cu_2(bim)_4(H_2O)\}_2\{[Cu(bim)_2]_2[Cu(bim)(H_2O)]_2Cu(H_2O)_2[Sr \subset P_6Mo^{V}_3Mo^{VI}_{15}O_{73}]_2\}\cdot 16H_2O$	3	Na_2MoO_4, CuC_2O_4, $SrCl_2$, H_3PO_4, NaOH, bim, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV/Vis, XPS, single-crystal XRD	electrocatalytic reduction of NO_2^-	129
$(H_3pytp)(H_2pytty)_2[\{Fe(H_2O)_4\}\{Sr \subset P_6Mo^{V}_3Mo^{VI}_{15}O_{73}\}]\cdot 5H_2O$	3	Na_2MoO_4, $FeSO_4$, $SrCl_2$, H_3PO_4, pytp, pytty, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV/Vis, XPS, single-crystal XRD	photocatalytic degradation of MB; electrocatalytic reduction of H_2O_2 and oxidation of dopamine	134
$(C_{10}H_{10}N_2)_{12}(PMo^{VI}_{12}O_{40})2(Sr \subset P_6Mo^{V}_3\ Mo^{VI}_{15}O_{73})2\cdot 9H_2O$	3	Na_2MoO_4, $SrCl_2$, H_3PO_4, 4,4'-bpy, H_2O	HT 160 °C, 4 d, pH = 3	EA, IR, TGA, UV/Vis, XPS, PXRD, single-crystal XRD	electrocatalytic reduction of NO_2^-	135
$\{H_3O\}_2\{Fe^{III}(2,2'\text{-bpy})_3\}_6\{Sr \subset P_6Mo^{V}_4Mo^{VI}_{14}O_{73}\}_2\cdot 9H_2O$	4	Na_2MoO_4, $FeSO_4$, $SrCl_2$, H_3PO_4, NaOH, 2,2'-bpy, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV/Vis, XPS, single-crystal XRD	electrocatalytic reduction of NO_2^-	129
$\{H_3O\}_4\{[Cd(phen)_2]_2Sr(H_2O)_5[Sr \subset P_6Mo^{V}_4Mo^{VI}_{14}O_{73}]\}\cdot H_2O$	4	Na_2MoO_4, $CdCO_3$, $SrCl_2$, H_3PO_4, NaOH, phen, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV/Vis, XPS, single-crystal XRD	electrocatalytic reduction of NO_2^-	129
$[Cu(phen)(H_2O)_3][\{Cu(phen)(H_2O)_2\}\{Cu(phen)(H_2O)\}_3\{Sr \subset P_6Mo^{V}_4Mo^{VI}_{14}O_{73}\}]\cdot 3H_2O$	4	Na_2MoO_4, $CuCl_2$, $SrCl_2$, H_3PO_4, phen, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV/Vis, XPS, single-crystal XRD, magnetometry	electrocatalytic reduction of H_2O_2	136
$[\{Mn(H_3pytty)(H_2O)_3\}_2\{Sr \subset P_6Mo^{V}_4Mo^{VI}_{14}O_{73}\}]\cdot 18H_2O$	4	Na_2MoO_4, $Mn(OAc)_2$, $SrCl_2$, H_3PO_4, pytty, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV/Vis, XPS, single-crystal XRD	photocatalytic degradation of MB; electrocatalytic reduction of H_2O_2 and oxidation of dopamine	134
$(H_2imi)_6(Himi)_4[\{Sr(H_2O)_4\}_2\{Sr \subset P_6Mo^{V}_4Mo^{VI}_{14}O_{73}\}_2]\cdot 17H_2O$	4	$(NH_4)_6Mo_7O_{24}$, H_3PO_4, $SrCl_2$, imi, H_2O	HT 160 °C, 4 d, pH = 3.5	EA, IR, TGA, UV/Vis, XPS, PXRD, single-crystal XRD	electrocatalytic reduction of NO_2^-	137
$(H_3bth)_4[\{Sr_{0.5}(H_2O)_{0.5}(H_2O)\}_2\{Sr(H_2O)_4\}_2\{M_{0.5}(H_2O)\}_2\{Sr \subset P_6Mo^{V}_4Mo^{VI}_{14}O_{73}\}_2]\cdot 5H_2O$, M = Cu, Ni	4	$(NH_4)_6Mo_7O_{24}$, $M(OAc)_2$, H_3PO_4, $SrCl_2$, bth, H_2O	HT 160 °C, 5 d, pH = 3.5	EA, IR, TGA, UV/Vis, XPS, BET, PXRD, single-crystal XRD	photocatalytic degradation of MB; electrocatalytic reduction of NO_2^-	138
$(H_2pytty)_2[\{Cd(H_2O)_4\}\{Cd(H_2O)_3(H_3pytty)\}\{Sr \subset P_6Mo^{V}_5Mo^{VI}_{13}O_{73}\}]\cdot 9H_2O$	5	Na_2MoO_4, $Cd(OAc)_2$, $SrCl_2$, H_3PO_4, pytty, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV/Vis, XPS, single-crystal XRD	photocatalytic degradation of MB; electrocatalytic reduction of H_2O_2 and oxidation of dopamine	134

	$(H_2pytty)_8[\{Mn(H_2pytty)(H_2O)_3\}\{Sr \subset P_6Mo^{V}_6Mo^{VI}_{12}O_{73}\}]_2 \cdot 16H_2O$	6	Na_2MoO_4, $Mn(OAc)_2$, $SrCl_2$, H_3PO_4, pytty, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV/Vis, XPS, single-crystal XRD	photocatalytic degradation of MB; electrocatalytic reduction of H_2O_2 and oxidation of dopamine	[134]
Ba^{2+}	$\{[Cu(2,2'\text{-bpy})(H_2O)]_4[Ba \subset P_6Mo^{V}_2Mo^{VI}_{16}O_{73}]\} \cdot 8H_2O$	2	Na_2MoO_4, $CuCl_2$, $BaCl_2$, H_3PO_4, NaOH, phen, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV/Vis, XPS, single-crystal XRD	electrocatalytic reduction of NO_2^-	[129]
			$\{M \subset (SO_3)_2(PhPO_3)_4Mo^{V/VI}_{18}O_{49}\}$				
Na^+	$(TBA)_5[Na(SO_3)_2(PhPO_3)_4Mo^{V}_4Mo^{VI}_{14}O_{49}] \cdot nMeCN$	4	Na_2MoO_4, HCl, $Na_2S_2O_4$, $PhPO_3H_2$, MeCN, TBABr	RT	EA, IR, TGA, UV/Vis, ^{31}P-NMR, single-crystal XRD	nr	[139, 140,]
			$\{B_2P_8Mo_{12}\}$				
	$(C_3N_2H_5)_8[Mo^{V}_5Mo^{VI}_7O_{22}(BO_4)_2(PO_4)_5(HPO_4)_3] \cdot nH_2O$ (n = 4)	5	MoO_3, Mo, H_3BO_3, $C_3N_2H_4$, H_3PO_4, HCl, H_2O	HT 165 °C, 5 d,	EA, IR, XPS, single-crystal XRD	nr	[141]
	$(C_3N_2H_5)_5[Mo^{V}_5Mo^{VI}_7O_{30}(BPO_4)_2(O_3P\text{-}Ph)_6] \cdot H_2O$	5	MoO_3, Mo, H_3BO_3, $PhPO_3H_2$, $C_3N_2H_4$, HCl, H_2O	HT 180 °C, 5 d, pH = 1	EA, IR, UV/Vis, EPR, single-crystal XRD	nr	[142]

nr – not reported

Methods

CV – cyclic voltammetry
DFT – density functional theory
EA – elemental analysis
EPR – electron paramagnetic resonance
HT – hydrothermal synthesis
IR – infrared spectroscopy
NMR – nuclear magnetic resonance
PXRD – powder X-ray diffraction
RT – room temperature
Single-crystal XRD – single-crystal X-ray diffraction
TGA – thermogravimetric analysis
UV-vis – ultraviolet-visible spectroscopy
XPS – X-ray photoelectron spectroscopy

Organic compounds

Ac – acetate
bpy – bipyridine
bib – 1,4-bis- (imidazole)butane
bim – 2,2'-biimidazole
bip – 1,5-bis(imidazol)pentane
bih – 1,6-bis(imidazol)hexane
bth – 1,6-bis(triazole)hexane
Bu – butyl
dmpip – 2,5-dimethylpiperazine
en – ethylenediamine
imi – imidazol
MB – methylene blue
Ph –phenyl
phen – 1,10-phenanthroline
pytp – 4'-(4"-pyridyl)-2,4':6',4"-terpyridine
pytty – 3 -(pyrazin-2-yl)-5-(1H-1,2,4-triazol-3-yl)-1,2,4-tria- zolyl
RhB – rhodamine B
TBA – tetrabutylammonium

Table S7 Selected details of synthesis and characterisation of Anderson-like alkoxo POVs and POMos. The compounds in each section are presented in in the ascending order of reduction degree.

Hetero-ion	Formula	No. of accepted e^-	Educts	Synthesis condition	Characterized *by*	Application	Ref.
X			**$\{XV^{IV}_6\}$**				
Li	$[LiV^{IV}_6O_6\{(OCH_2CH_2)_2N(CH_2CH_2OH)\}_6]Cl{\cdot}LiCl$	6	$[NH_4]_6[V^V_{10}O_{28}]$, LiCl, CH_3CN, C_2H_5OH, $\{C_2H_4OH\}_3N$	HT 145 °C, 67 h	EA, IR, TGA, single-crystal XRD, magnetometry	nr	[143]
Na	$[NaV^{IV}_6O_6\{(OCH_2CH_2)_2N(CH_2CH_2OH)\}_6]Cl{\cdot}H_2O$	6	$[NH_4]_6[V^V_{10}O_{28}]{\cdot}6H_2O$, NaCl, CH_3CN, C_2H_5OH, $\{C_2H_4OH\}_3N$	HT 145 °C, 24 h	EA, IR, TGA, single-crystal XRD, magnetometry	nr	[143]
	$[NaV^{IV}_6O_6\{(OCH_2CH_2)_2NH\}_6]{\cdot}(OH)_{0.5}Cl_{0.5}{\cdot}(HOCH_2CH_2)_2N(CH_2CH_2NH_2)$	6	$[NH_4]_6[V^V_{10}O_{28}]{\cdot}6H_2O$, NaCl,${\cdot}(HOCH_2CH_2)_2NCH_2CH_2NH_2$	HT 145 °C, 24 h	EA, IR, UV/Vis, TGA, CV, single-crystal XRD	nr	[144]
Mg	$[MgV^{IV}_6O_6\{(OCH_2CH_2)_2N(CH_2CH_2OH)\}_6]2Br{\cdot}H_2O$	6	$[^nBu_4N]_6[V_{10}O_{28}]$, MgBr, CH_3CN, C_2H_5OH, $\{C_2H_4OH\}_3N$	HT 155 °C, 6 h	EA, IR, TGA, single-crystal XRD, magnetometry	nr	[143]
Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}	$[M^{II}V^{IV}_6O_6\{(OCH_2CH_2)_2N(CH_2CH_2OH)\}_6]2Cl$, M = Mn, Fe, Co, Ni	6	$[NH_4]_6[V_{10}O_{28}]{\cdot}6H_2O$, MCl_2, CH_3CN, C_2H_5OH, $\{C_2H_4OH\}_3N$	HT 145 °C, 26 h	EA, IR, TGA, single-crystal XRD, magnetometry	nr	[143]
Mn^{II}	$[Mn^{II}V^{IV}_6O_6\{(OCH_2CH_2)_2N(CH_2CH_2OH)\}_6]Cl_2$	6	$(HOCH_2CH_2)_3N$, $[^nBu_4N]_3[H_3V^V_{10}O_{28}]$, $MnCl_2$ $C_6H_3(COOH)_3$-1,3,5, MeCN, MeOH	HT 145 °C, 24 h	EA, IR, single-crystal XRD,	nr	[145]
V^V	$[NH_2Et_2]_4\{[V^{IV}_6O_6(OCH_3)_9(V^VO_3)(H_2O)]_4(L)_6\}$(Solvent), L = BDC, BDC-$NH_2$; Solvent = DEF, CH_3OH	6	VCl_3, H_2L, DEF, CH_3OH, H_2O	HT 130 °C, 2 d	EA, IR, TGA, XPRD, single-crystal XRD, magnetometry	nr	[146]
S^{VI}	$(NH_2Et_2)_8\{[V^{IV}_6O_6(OCH_3)_9(SO_4)]_4(L)_6\}$(Solvent), L = BDC, BDC-$NH_2$, BDC-Br; Solvent = DEF	6	$VOSO_4$, H_2L, DEF, CH_3OH, H_2O	HT 130 °C, 2 d	EA, IR, TGA, XPS, single-crystal XRD, magnetometry	nr	[147]
C^{IV}	$(NH_4)_5[(V^{IV}O)_6(CO_3)_4(OH)_9]{\cdot}10H_2O$	6	$VOCl_2$, NH_4HCO_3, CO_2	pH = 7.6 – 7.8	EA, IR, single-crystal XRD	nr	[148]
–	$[V^{IV}_6O_6\{(OCH_2CH_2)_2N(CH_2CH_2OH)\}_6]{\cdot}0.5CH_3CN$	6	$[NH_4]_6[V^V_{10}O_{28}]$, $(HOCH_2CH_2)_3N$, EtOH, MeCN	HT 145 °C, 27 h	EA, IR,UV-Vis, TGA, single-crystal XRD,	nr	[149]
X			**$\{X_4Mo^V_6\}$ and dimers $\{X_4Mo^V_6\}_2$**				
P^V	$(PPh_4)_2[(H_3O)_2NaMo^V_6P_4O_{24}(OH)_7]{\cdot}5H_2O$	6	Na_2MoO_4, Mo, H_3PO_4, PPh_4Br, H_2O	HT 130 °C, 1 d	EA, IR, single-crystal XRD	nr	[150]
	$[Et_4N]_6[Na_{14}\{Mo^V_6P_4O_{24}(OH)_7\}_4P(OH)_3]{\cdot}xH_2O$	6	Na_2MoO_4, Mo, H_3PO_4, Et_4NOH, H_2O	HT 200 °C, 3 d	EA, IR, single-crystal XRD	nr	[151]
	$Na_2Cd_3(Mo_2O_4OH)_6(PO_4)_2(PO_3OH)_6[N(CH_3)_4]_4{\cdot}10H_2O$ + $Cd_9(Mo_2O_4OH)_{12}(PO_4)_6(PO_3OH)_{10}[N(CH_3)_4]_8{\cdot}15H_2O$	6	Na_2MoO_4, Mo, CdO, H_3PO_4, $(CH_3)_4NOH$, and H_2O	HT 220 °C, 1.5 d	EA, IR, single-crystal XRD	nr	[152]
	$Na_8(Mo^V_2O_4OH)_3(PO_4)_3(PO_3OH){\cdot}12.25H_2O$	6	Na_2MoO_4, Mo, H_3PO_4, NaOH, and H_2O	HT 220 °C, 1.5 d	EA, IR, TGA, single-crystal XRD	nr	[153]

	$Na_4Cs_4Cl_2[H_6P_4Mo^{V}_6S_6O_{25}]\cdot 13H_2O$	6	$K_{2.6}(NMe_4)_{0.4}I_3[Mo_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6]$, NaH_2PO_4, HCl, CsCl	50 °C, pH = 5	EA, IR, TGA, ^{31}P NMR, single-crystal XRD	nr	[154]
	$(4,4'\text{-}H_2bpy)[Ni(4,4'\text{-}bpy)(H_2O)_2Ni_{0.5}\text{-}Mo^{V}_6(OH)_3O_{12}(HPO_4)_4]\cdot 2H_2O$	6	$NiSO_4$, MoO_3, Mo, $(NH_4)H_2PO_4$, 4,4′-bipyridine, H_2O	HT 160 °C, 3 d	EA, IR, TGA, single-crystal XRD, magnetometry	nr	[155]
	$(TMA)_2(Cat)_2[M_n\{Mo^{V}_6O_{15}(HPO_4)(H_2PO_4)_3\}_2]\cdot xH_2O$ (M = Zn^{II}, n = 3, Cat = H_3O+; M = Fe^{III}, n = 2, Cat = NH_4^+)	12	Na_2MoO_4, Mo, ZnO or $FeCl_3$, $(CH_3)_4NOH$, H_3PO_4, and H_2O	HT 200 °C, 6 d	EA, IR, single-crystal XRD	nr	[156, 157]
	$[Et_4N]_2Na_3(H_3O)_4\{(Na[(Mo^{V}_6O_{15}(O_3PC_6H_5)(HO_3PC_6H_5)_3]_2\}\cdot\sim 14H_2O$	12	Na_2MoO_4, Mo, $C_6H_5PO_3H_2$, $(CH_3)_4NOH$, H_3PO_4, and H_2O	HT 200 °C, 3 d	EA, IR, single-crystal XRD	nr	[158]
	$(NH_4)_5Na_4\{Na[Mo^{V}_6O_{12}(OH)_3(O_3PC_6H_5)_4]_2\}\cdot 6H_2O$	12	Na_2MoO_4, Mo, $C_6H_5PO_3H_2$, KCl, NH_4Cl, and H_2O	HT 180 °C, 3 d	EA, IR, single-crystal XRD	nr	[159]
	$(C_{15}H_{28}N_2)_4(C_9H_6O_6)_1[H_{15}Mo^{V}_{12}NaO_{62}P_8]\cdot 10H_2O$	12	Na_2MoO_4, 1,3,5-benzenetricarboxylic acid, H_3PO_4, $Na_2S_2O_4$	2 h, pH = 3.5	EA, IR, TGA, single-crystal XRD	nr	[160]
	$(NH_3CH_2CH_2NH_3)_{10}(H_3O)_3(H_5O_2)Na_2[MnMo^{V}_{12}O_{24}(OH)_6(PO_4)_4(PO_3OH)_4][MnMo^{V}_{12}O_{24}(OH)_6(PO_4)_6(PO_3OH)_2]\cdot 9H_2O$	12	$MnSO_4$, Na_2MoO_4, H_3PO_4, Mo, $H_2N(CH_2)_2NH_2$, H_2O	HT 250 °C, 51 h	EA, IR, TGA, DSC, single-crystal XRD	oxidation of acetaldehyde with H_2O_2	[161]
	$[\{K(H_2O)\}_{12}\{CoMo^{V}_{12}O_{24}(OH)_6(HPO_4)_4(PO_4)_4\}]$	12	$(NH_4)_6Mo_7O_{24}\cdot H_2O$, $Co(CH_3COOH)_2\cdot 2H_2O$, $CH_3COOK\cdot H_2O$, 2,2′-bpy, H_3PO_4, H_2O	HT 160 °C, 4 d	EA, IR, TGA, UV-vis, single-crystal XRD	reduction of NO_2^- and oxidation of ascorbic acid	[162]
	$(H_2bpp)_6\{Ni[Mo^{V}_6O_{13}(OH)_2(HPO_4)_3(H_2PO_4)]_2\}_2\cdot 13H_2O$	12	Na_2MoO_4, $NiCl_2$, H_3PO_4, bpp, H_2O	HT 180 °C, 5 d, pH = 1.5	EA, IR, TGA, UV-vis, PXRD, single-crystal XRD	reduction of $[Fe(CN)_6]^{3-}$	[163]
	$(H_2bpp)_5\{Cd[Mo^{V}_6O_{15}(HPO_4)_3(H_2PO_4)]_2\}\{Cd[Mo^{V}_6O_{15}(HPO_4)_42\}\cdot 10H_2O$	12	Na_2MoO_4, $CdCl_2$, H_3PO_4, bpp, H_2O	HT 180 °C, 5 d, pH = 1.5	EA, IR, TGA, UV-vis, PXRD, single-crystal XRD	reduction of $[Fe(CN)_6]^{3-}$	[163]
	$(H_2bpp)_2[Cd(H_2O)Cd(H_2O)_2]_2\{Cd[Mo^{V}_6O_{12}(OH)_3(HPO_4)_2(PO_4)_2]_2\}\cdot 8H_2O$	12	Na_2MoO_4, $CdCl_2$, H_3PO_4, bpp, H_2O	HT 180 °C, 5 d, pH = 0.8	EA, IR, TGA, UV-vis, PXRD, single-crystal XRD	reduction of $[Fe(CN)_6]^{3-}$	[163]
As^{V}	$Na_{1.5}Cs_4Cl_{0.5}[H_7As_4Mo_6S_6O_{25}]\cdot 13H_2O$	6	$K_{2.6}(NMe_4)_{0.4}I_3[Mo_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6]$, H_3AsO_4, HCl, NaOH CsCl	50 °C, pH = 4	EA, IR, TGA, ^{31}P NMR, single-crystal XRD	nr	[154]
C^{IV}	$(NH_4)_5[(Mo^{V}_2O_4)_3(CO_3)_4(OH)_3]\cdot 0.5CH_3OH$	6	NH_4HCO_3, $Mo^{V}Cl_5$, H_2O	pH = 8	EA, IR, single-crystal XRD	nr	[164]
			$\{Mo^{V}_{16}P_{24/26}\}$				
	$[(Mo^{V}_2O_4)_8(HPO_4)_{14}(PO_4)_{10}\{Co_{22}Cl_2(H_2O)_{42}\}]\cdot 28H_2O$	16	Na_2MoO_4, Mo, H_3PO_4, $CoCl_2$, H_2O, HCl	HT 180 °C, 3 d, pH = 2	EA, IR, single-crystal XRD, magnetometry	nr	[165]
	$[(Mo^{V}_2O_4)_8(HPO_4)_{14}(PO_4)_{10}\{Co_{19}Na_4(H_2O)_{34}\}]\cdot 14H_2O$	16	Na_2MoO_4, Mo, H_3PO_4, $CoCl_2$, H_2O, HCl	HT 180 °C, 3 d, pH = 3.9	EA, IR, single-crystal XRD, magnetometry	nr	[165]
	$Na_6Ni_6[(Mo^{V}_2O_4)_8Ni_{16}(H_2PO_4)_4(HPO_4)_{10}(PO_4)_{12}(OH)_6(H_2O)_8]\cdot 66H_2O$	16	Na_2MoO_4, Mo, H_3PO_4, $NiCl_2$, H_2O, HCl	HT 130 °C, 9 d,	EA, IR, single-crystal XRD, magnetometry	nr	[166]

				pH = 3.3		
$[H_2en]_3Na_4[Ni(H_2O)_3][H_{30}(Mo^{V}_{16}O_{32})Ni_{14}(PO_4)_{26}O_2(OH)_4(H_2O)_8]\cdot 8H_2O$	16	Na_2MoO_4, H_3PO_4, $Ni(CH_3COO)_2$, H_2O, ethylenediaminetetraacetic acid	HT 180 °C, 7 d, pH = 3-4	EA, IR, single-crystal XRD, magnetometry	nr	[167]
$Na_2[Co(H_2O)_6][(Mo_{16}O_{32})Co_{16}(PO_4)_4(HPO_4)_{16}(H_2PO_4)_4(OH)_4(C_{10}H_8N_2)_4(C_5H_4N)_2(H_2O)_6]_3\cdot 4H_2O$	16	Na_2MoO_4, H_3PO_4, 4.4'-bpy, pyridine, H_2O, NaOH	HT 165 °C, 5 d, pH = 2.5	EA, IR, TGA, single-crystal XRD, magnetometry	nr	[168]

nr – not reported

Methods

CV – cyclic voltammetry
EA – elemental analysis
EPR – electron paramagnetic resonance
HT – hydrothermal synthesis
IR – infrared spectroscopy
NMR – nuclear magnetic resonance
PXRD – powder X-ray diffraction
RT – room temperature
Single-crystal XRD – single-crystal X-ray diffraction
TGA – thermogravimetric analysis
UV-vis – ultraviolet-visible spectroscopy
XPS – X-ray photoelectron spectroscopy

Organic compounds

bpp – 1,3-bis(4-pyridyl)propane
bpy – bipyridine
DEF - N,N-diethylformamide
Et – ethyl
H_2BDC – 1,4-benzenedicarboxylate
$H_2BDC–NH_2$ – 2-amino-1,4-benzenedicarboxylate
Me – methyl
TMA – tetramethylammonium

References

1 Sanchez, C., Livage, J., Launay, J. P., Fournier, M. & Jeannin, Y. Electron delocalization in mixed-valence molybdenum polyanions. *J. Am. Chem. Soc.* **104**, 3194–3202 (1982).

2 Che, M., Fournier, M. & Launay, J. P. The analog of surface molybdenyl ion in Mo/SiO_2 supported catalysts: The isopolyanion $Mo_6O_{19}^{3-}$ studied by EPR and UV-visible spectroscopy. Comparison with other molybdenyl compounds. *J. Chem. Phys.* **71,** 1954–1960 (1979).

3 Feng, W.-L. Theoretical investigation of EPR and optical spectra of Mo(V) in $[Mo_6O_{19}][N(C_4H_9)_4]_3$ salt. *J. Magn. Magn. Mater.* **324,** 4061–4063 (2012).

4 Yamase, T. & Kurozumi, T. Photoreduction of Polymolybdates(VI) in Aqueous Solutions containing Acetic Acid. *J. Chem. Soc., Dalt. Trans.* 2205–2209 (1983).

5 Yamase, T. Photochemical studies of the alkylammonium molybdates. Part 6. Photoreducible octahedron site of $[Mo_7O_{24}]^{6-}$ as determined by electron spin resonance. *Dalton Trans.*, 1987–1991 (1982).

6 Wang, L. *et al.* χ-octamolybdate $[Mo^{V}_4Mo^{VI}_4O_{24}]^{4-}$: An unusual small polyoxometalate in partially reduced form from nonaqueous solvent reduction. *Chem. - A Eur. J.* **17**, 4796–4801 (2011).

7 Yamase, T. Anti-tumor, -viral, and -bacterial activities of polyoxometalates for realizing an inorganic drug. *J. Mater. Chem.* **15,** 4773 (2005).

8 Ogata, A. *et al.* Antitumour effect of polyoxomolybdates: induction of apoptotic cell death and autophagy in in vitro and in vivo models. *Br. J. Cancer* **98,** 399–409 (2008).

9 Yamase, T. & Ishikawa, E. Photoreductive self-assembly from $[Mo^{VI}_7O_{24}]^{6-}$ to Anti-Tumoral $[H_2Mo^{V}_{12}O_{28}(OH)_{12}(Mo^{VI}O_3)_4]^{6-}$ in aqueous media. *Bull. Chem. Soc. Jpn.* **81**, 983–991 (2008).

10 Khan, M. I. *et al.* Cation Inclusion within the mixed-valence polyanion cluster $[(Mo^{VI}O_3)_4Mo^{V}_{12}O_{28}(OH)_{12}]^{8-}$: syntheses and structures of $(NH_4)_7[NaMo_{16}(OH)_{12}O_{40}]4H_2O$ and $(Me_2NH_2)_6[H_2Mo_{16}(OH)_{12}O_{40}]$. *Angew. Chemie Int. Ed.* ***32****, 1780–1782 (1993)*.

11 Chen, W.-P., Sang, R.-L., Wang, Y. & Xu, L. An unprecedented $[Mo^{IV}_3O_4]$-incorporated polyoxometalate concomitant with MoO_2 nucleophilic addition. *Chem. Commun.* **49**, 5883–5885 (2013).

12 Long, D. L., Kögerler, P., Farrugia, L. J. & Cronin, L. Restraining symmetry in the formation of small polyoxomolybdates: Building blocks of unprecedented topology resulting from 'shrink-wrapping' $[H_2Mo_{16}O_{52}]^{10-}$ type clusters. *Angew. Chem.??? - Int. Ed.* **42**, 4180–4183 (2003).

13 Proust, A., Robert, F., Gouzerh, P., Chen, Q. & Zubieta, J. Reduced nitrosyl polyoxomolybdates with the hitherto unknown decamolybdate Y structure: Preparation and crystal and electronic structures of the two-electron reduced $[Mo_{10}O_{25}(OMe)_6(NO)]^{-}$ and the four-electron reduced $[Mo_{10}O_{24}(OMe)_7(NO)]^{2-}$. *J. Am. Chem. Soc.* **119**, 3523–3535 (1997).

14 Khan, I. M., Cevik, S., Doedens, R. J. & O'Connor, C. J. Hydrothermal synthesis and characterization of mixed-valence hexatungstates: crystal structures of $[(C_2H_5)_4N]_3[W^{V}W_5^{VI}O_{19}]\cdot0.5H_2O$ and [H3N(CH2)2NH3]2 $[W^{V}W_5^{VI}O_{19}]\cdot[H_2N(CH_2)_2NH_2]Cl\cdot8H_2O$. *Inorg. Chim. Acta* **277**, 69–75 (1998).

15 Yang, W. B. *et al.* Synthesis, structural characterization, and magnetic properties of a new charge-transfer salt composed of polyoxotungstate acceptors $[W^{V}W^{VI}_5O_{19}]^{3-}$ and cationic ferrocenyl $CpFe^{+}$ Cp donors. *J. Clust. Sci.* **14,** 421–430 (2003).

16 Pope, M. T. & Varga, G. M. Heteropoly Blues. I. Reduction Stoichiometries and Reduction Potentials of Some 12-Tungstates. *Inorg. Chem.* **5**, 1249–1254 (1966).

17 Varga, G. M., Papaconstantinou, E. & Pope, M. T. Heteropoly blues. IV. Spectroscopic and magnetic properties of some reduced polytungstates. *Inorg. Chem.* **9**, 662–667 (1970).

18 Jeannin, Y., Launay, J. P. & Sedjadi, M. A. S. Crystal molecular structure of the six-electron-reduced form of metatungstate $Rb_4H_8(H_2W_{12}O_{40})(H_2O)_{18}$ occurrence of a metal-metal bonded subcluster in a heteropolyanion framework. *Inorg. Chem.* **19**, 2933–2935 (1980).

19 Bond, A. M., Boskovic, C., Sadek, M. & Brownlee, R. T. C. Electrosynthesis and solution structure of six-electron reduced forms of metatungstate, $[H_2W_{12}O_{40}]^{6-}$. *J. Chem. Soc. Dalt. Trans.* **2**, 187–196 (2001)

20 Christian, J. B., Smith, S. P. E., Whittingham, M. S. & Abruña, H. D. Tungsten based electrocatalyst for fuel cell applications. *Electrochem. Commun.* **9**, 2128–2132 (2007).

21 Launay, J. P. Reduction de l'ion metatungstate: Stades eleves de reduction de $H_2W_{12}O_{40}^{6-}$, derives de l'ion $HW_{12}O_{40}^{7-}$ et discussion generale. *J. Inorg. Nucl. Chem.* **38**, 807–816 (1976).

22 Smith, S. P. E. & Christian, J. B. Mechanism of the coupled 24-electron reduction and transformations among the 'blues', the 'browns' and the 'reds' of ammonium metatungstate. *Electrochim. Acta* **53**, 2994–3001 (2008).

23 Kazansky, L. P. & Launay, J. P. X-ray photoelectron study of mixed valence metatungstate anions. *Chem. Phys. Lett.* **51**, 242–245 (1977).

24 Yamase, T. Involvement of hydrogen-bonding protons in delocalization of the paramagnetic electron in a single crystal of photoreduced decatungstate. *J. Chem. Soc. Dalton Trans.*, 1597–1604 (1987).

25 Sasaki, Y., Yamase, T., Ohashi, Y. & Sasada, Y. Structural retention of decatungstate upon photoreduction. *Bull. Chem. Soc. Jpn.* **60**, 4285–4290 (1987).

26 Chemseddine, A., Sanchez, C., Livage, J., Launay, J. P. & Fournier, M. Electrochemical and photochemical reduction of decatungstate: a reinvestigation. *Inorg. Chem.* **23**, 2609–2613 (1984).

27 Duncan, D. C. & Fox, M. A. Early events in decatungstate photocatalyzed oxidations: a nanosecond laser transient absorbance reinvestigation. *J. Phys. Chem. A* **5639**, 4559–4567 (1998).

28 Müller, A., Meyer, J., Bögge, H., Stammler, & Botar, A. A. Cis-/Trans-Isomerie bei Bis-(trisa1koxy)-hexavanadaten: cis-$Na_2[V^{IV}{}_6O_7(OH)_6\{(OCH_2)_3CCH_2OH\}_2]\cdot 8H_2O$, cis-$(CN_3H_6)_3[V^{IV}V^{V}{}_5O_{13}\{(OCH_2)CCH_2OH\}_2]\cdot 4{,}5H_2O$ und trans-$(CN_3H_6)_2[V^{V}{}_6O_{13}\{(OCH_2)CCH_2OH\}_2]\cdot H_2O$. *Z. Anorg. Allg. Chem.* **621**, 1818–1831 (1995).

29 Daniel, C. & Hartl, H. Neutral and cationic V^{IV}/V^{V} mixed-valence alkoxo-polyoxovanadium clusters $[V_6O_7(OR)_{12}]^{n+}$ (R = -CH_3, -C_2H_5): Structural, cyclovoltammetric and IR-spectroscopic investigations on mixed valency in a hexanuclear core. *J. Am. Chem. Soc.* **127**, 13978–13987 (2005).

30 Xu, X. *et al.* A combined crystallographic analysis and ab initio calculations to interpret the reactivity of functionalized hexavanadates and their inhibitor potency toward Na^+/K^+-ATPase. *J. Inorg. Biochem.* **161,** 27–36 (2016).

31 Qin, C. & Zubieta, J. Structural investigations of the hexavanadium core $\{V_6O_{19}\}$ in 'oxidized', mixed valence and 'reduced' clusters of the type $[V^{V}{}_{6-n}V^{IV}{}_nO_{13-n}(OH)_n\{(OCH_2)_3CR\}_2]^{2-}$, n = 0, 3 and 6. *Inorg. Chim. Acta* **198–200**, 95–110 (1992).

32 Li, F., Vangelder, L. E., Brennessel, W. W. & Matson, E. M. Self-assembled, iron-functionalized polyoxovanadate alkoxide clusters. *Inorg. Chem.* **55**, 7332–7334 (2016).

33 Spandl, J., Daniel, C., Brüdgam, I. & Hartl, H. Synthesis and structural characterization of redox-active dodecamethoxoheptaoxohexavanadium clusters. *Angew. Chem. Int. Ed.* **42**, 1163–1166 (2003).

34 Khan, M. I. *et al.* Polyoxo alkoxides of vanadium - the structures of the decanuclear vanadium(IV) clusters $[V_{10}O_{16}(CH_3CH_2C(CH_2O)_3)_4]^{4-}$ and $[V_{10}O_{13}(CH_3CH_2C(CH_2O)_3)_5]$. *J. Am. Chem. Soc.* **114**, 3341–3346 (1992)

35 Daniel, C. & Hartl, H. Neutral and cationic VIV/VV mixed-valence alkoxo-polyoxovanadium clusters $[V_6O_7(OR)_{12}]^{n+}$ (R = -CH_3, -C_2H_5): Structural, cyclovoltammetric and IR-spectroscopic investigations on mixed valency in a hexanuclear core. *J. Am. Chem. Soc.* **127**, 13978–13987 (2005).

36 Augustyniak-Jablokow, M. A., Daniel, C., Hartl, H., Spandl, J. & Yablokov, Y. V. Exchange interactions and electron delocalization in the mixed-valence cluster $V_4{}^{IV}V_2{}^{V}O_7(OC_2H_5)_{12}$. *Inorg. Chem.* **47**, 322–332 (2008).

37 Chen, Q. *et al.* Coordination-Compounds of Polyoxovanadates With a Hexametalate Core - Chemical and Structural Characterization of $[V^{V}{}_6O_{13}\{(OCH_2)_3CR\}_2]^{2-}$, $[V^{V}{}_6O_{11}(OH)_2\{(OCH_2)_3CR\}_2]$, $[V^{IV}{}_4V^{V}{}_2O_9(OH)_4\{(OCH_2)_3CR\}_2]^{2-}$, and $[V^{IV}{}_6O_7(OH)_6\{(OCH_2)_3CR\}_2]^{2-}$. *J. Am. Chem. Soc.* **114**, 4667–4681 (1992).

38 Khan, M. I. *et al.* Hydrothermal synthesis and characterization of hexavanadium polyoxo alkoxide anion clusters - crystal-structures of the vanadium(IV) species $Ba[V_6O_7(OH)_3\{(OCH_2)_3CCH_3\}_3]\cdot 3H_2O$ and $Na_2[V_6O_7\{(OCH_2)_3CCH_2CH_3\}_4]$, of the mixed-valence complex $(Me_3NH)[V^{IV}{}_5V^{V}O_7(OH)_3\{(OCH_2)_3CCH_3\}_3]$ and of the fluoro derivative $Na[V_6O_6F(OH)_3\{(OCH_2)_3CCH_3\}_3]\cdot 3H_2O$. *Inorg. Chem.* **32**, 2929–2937 (1993).

39 Aronica, C. *et al.* A mixed-valence polyoxovanadate(III,IV) cluster with a calixarene cap exhibiting ferromagnetic V(III)-V(IV) interactions. *J. Am. Chem. Soc.* **130**, 2365–2371 (2008).

40 Och, R., Khan, M. I., Chen, Q., Goshom, D. P. & Zubieta, J. Polyoxo Alkoxide clusters of vanadium: structural characterization of the decavanadate core in the "fully reduced" vanadium(IV) species $[V_{10}O_{16}\{(OCH_2)_3CCH_2CH_3\}_4]^{4-}$ and $[V_{10}O_{14}\{(OCH_2)_3CCH_2OH\}_4]^{2-}$ and in the mixed-valence clusters $[V^{IV}{}_8V^{V}{}_2O_{16}\{(OCH_2)_3CR\}_4]^{2-}$ (R = -CH_2CH_3, -CH3). *Inorg. Chem.* **32**, 672–680 (1993).

41 Hayashi, Y., Miyakoshi, N., Shinguchi, T. & Uehara, A. A Stepwise Growth of Polyoxovanadate by Reductive Coupling Reaction with Organometallic Palladium Complex: Formation of $[\{(\eta_3\text{-}C_4H_7)Pd\}_2V_4O_{12}]^{2-}$, $[V_{10}O_{26}]^{4-}$ and $[V_{15}O_{36}(Cl)]^{4-}$. *Chem. Lett.* **36**, 170–171 (2001).

42 Heitner-Wirguin, C. & Selbin, J. A new mixed valence compound of vanadium. *J. Inorg. Nucl. Chem.*, **30**, 3181–3188 (1968).

43 Bino, A., Cohen S. & Heitner-Wirguin, C. Molecular structure of a mixed-valence isopolyvanadate. *Inorg. Chem.*, **21**, 429–431 (1982).

44 Forster, J., Rösner, B., Khusniyarov, M. M. & Streb, C. Tuning the light absorption of a molecular vanadium oxide system for enhanced photooxidation performance. *Chem. Commun.* **47,** 3114–3116 (2011).

45 Okaya, K., Kobayashi, T., Koyama, Y., Hayashi, Y. & Isobe, K. Formation of vv lacunary polyoxovanadates and interconversion reactions of dodecavanadate species. *Eur. J. Inorg. Chem.* 5156–5163 (2009).

46 Baxter, S. M. & Wolczanski, P. T. Improved synthesis, redox chemistry, and magnetism of the mixed-valence isopolyanion of vanadate $V_{10}O_{26}{}^{4-}$. *Inorg. Chem.* **28**, 3263–3264 (1989).

47 Tian, A.-X. *et al.* A series of polyoxometalate-based compounds including infinite Ag belts and circles constructed by two tolyl-1H-tetrazole isomers. *RSC Adv.* **5**, 53757–53765 (2015).

48 Zhang, Q.-Z. *et al.* Synthesis and Structure of two Keggin-type Heteropolyanions: $[VMo_{12}O_{40}]_n{}^{3n-}$ (1) and $[H_3PMo^{V}Mo^{VI}{}_{11}O_{40}]^{1-}$ (2). *J. Clust. Sci.* **14**, 381–390 (2003).

49 Qi, M.-L. *et al*. Three new three-dimensional organic–inorganic hybrid compounds based on $PMo_{12}O_{40}{}^{n-}$ (n = 3 or 4) polyanions and Cu^{I}–pyrazine/Cu^{I}–pyrazine–Cl porous coordination polymers. *Dalt. Trans.* **42**, 7586–7594 (2013).

50 Tian, A.-X. *et al.* Subtly tuning one N site of benzyl-1H-triazole ligands to build mono-nuclear subunits and tri-nuclear clusters to modify polyoxometalates. *CrystEngComm* **17**, 5569–5578 (2015).

51 Dai, L. *et al.* Hydrothermal Synthesis and crystal structure of two new α-keggin derivatives decorated by transition metal complexes. *Transit. Met. Chem.* **31**, 340–346 (2006).

52 Bakri, R. *et al.* Rational addition of capping groups to the phosphomolybdate Keggin anion $[PMo_{12}O_{40}]^{3-}$ by mild, non-aqueous reductive aggregation. *Chem. Comm.* **48**, 2779–2781 (2012).

53 Yuan, M. *et al.* Modified polyoxometalates: Hydrothermal syntheses and crystal structures of three novel reduced and capped Keggin derivatives decorated by transition metal complexes. *Inorg. Chem.* **42**, 3670–3676 (2003).

54 Barrows, J. N., Jameson, G. B. & Pope, M. T. Structure of a heteropoly blue. The four-electron reduced β-12-molybdophosphate anion. *J. Am. Chem. Soc.* **107**, 1771–1773 (1985).

55 Zhou, Y. *et al.* Synthesis and the third-order optical nonlinearities of two novel charge- transfer complexes of a heteropoly blue type $(C_9H_7NO)_4H_7PMo_{12}O_{40}\cdot 3H_2O$ (C_9H_7NO = quinolin-8-ol) and $(phen)_3H_7PMo_{12}O_{40}\cdot CH_3CN\cdot 3H_2O$ (phen=1,10-phenanthroline) *Polyhedron* **18**, 1419–1423 (1999).

56 Zhang, C. *et al.* A hybrid polyoxometalate-organic molecular catalyst for visible light driven water oxidation. *Chem. Commun.* **50**, 11591–4 (2014).

57 Dong, B.-X. *et al.* Synthesis, crystal structure and electrochemical properties of a new 2D network containing linear $\{\varepsilon\text{-}H_2PMo_8^{V}Mo_4^{VI}O_{40}Zn_4\}_\infty$ inorganic chain. *J. Clust. Sci.* **27**, 361–371 (2016).

58 Dong, B. X. *et al.* A new 2D network constructed from the extension of transition-metal-grafted ε-Keggin polyoxoanion by a bridging organic carboxylate. *J. Clust. Sci.* **26**, 1595–1605 (2015).

59 Chen, W. & Mi, J. A new redox-based approach for synthesizing a mixed-valence hybrid polymolybdate uncommonly bicapped by Cr (III) coordination complexes. *Polyhedron* **85**, 117–123 (2015).

60 Vu, T., Bond, A. & Hockless, D. Electrochemical synthesis and structural and physical characterization of one-and two-electron-reduced forms of $[SMo_{12}O_{40}]^{2-}$. *Inorg. Chem.* **40**, 65–72 (2001).

61 Wang, W., Xu, L., Gao, G., Liu, L. & Liu, X. The first ε-Keggin core of molybdogermanate in extended architectures of nickel(II) with N-donor ligands: Syntheses, crystal structures and magnetic properties. *CrystEngComm* **11,** 2488–2493 (2009).

62 Cui, X. B., Zheng, S. T. & Yang, G. Y. First Nickel(II) cation inclusion within the mixed-valence polyoxomolybdate capped with four NiII(en)(H2O) groups: Hydrothermal synthesis and structure of $[Mo^{V}_8Mo^{VI}_4O_{30}(\mu_2\text{-}OH)_6(Ni^{II}O_4)\{Ni^{II}(en)(H_2O)\}_4]$. *Z. Anorg. Allg. Chem* **631**, 642–644 (2005).

63 Müller, A. *et al.* $[Mo(V)_{12}O_{30}(\mu_2\text{-}OH)_{10}H_2\{Ni(II)(H_2O)_3\}_4]$, a highly symmetrical ε-Keggin unit capped with four Ni(II) centers: Synthesis and magnetism. *Inorg. Chem.* **39**, 5176–5177 (2000).

64 Li, N. & Huang, R. Journal of Solid State Chemistry Six new inorganic – organic hybrids based on rigid triangular ligands : Syntheses , structures and properties. *J. Solid State Chem.* **233,** 320–328 (2016).

65 Zhao, C. *et al.* A molecular crown analogue templated by Keggin polyanions: synthesis, structure, and electrochemical and luminescent properties. *Z. Naturforsch., B: Chem. Sci. B* **70**, 547–553 (2015).

66 Bai, L., Lin, B. Z., Huang, X. F., Chen, Z. J. & Cao, X. G. Hydrothermal synthesis, crystal structures and electrochemical properties of two phosphatotungstates containing keggin clusters, $[Cu(2,2'\text{-bipy})_2]_5[PW_{12}O_{40}]\cdot 2H_2O$ and $(Hpip)_3[PW_{12}O_{40}]$. *J. Clust. Sci.* **19**, 561–572 (2008).

67 Zhang, X. *et al.* Steric hindrance-dependent rational design and synthesis of three new Keggin-based supramolecular networks. *Dalt. Trans.* 9198–9206 (2009).

68 Wang, Z., Gao, S., Xu, L., Shen, E. & Wang, E. Synthesis and structural characterization of a tungstophosphate heteropoly blue. *Polyhedron*, **15**, 1383–1388 (1996).

69 Zhang, H. *et al.* Two unusual organic–inorganic hybrid 3-D frameworks based on Keggin-type heteropoly blue anion-chains, 40-membered macrocycles, and sodium linker units. *CrystEngComm* **16**, 8449–8456 (2014).

70 Wang, J., Shen, Y. & Niu, J. Hydrothermal synthesis and crystal structure of a novel compound supported by α-Keggin units $[Cu(2,2'\text{-bipy})_2]\{W^{V}_{40}[Cu(2,2'\text{-bipy})_2]_2\}\cdot 2H_2O$. *J. Coord. Chem.* **59**, 1007–1014 (2006).

71 Geletii, Y. V *et al.* Electron exchange between alpha-Keggin tungstoaluminates and a well-defined cluster-anion probe for studies in electron transfer. *Inorg. Chem.* **44**, 8955–66 (2005).

72 Casañ-Pastor, N., Gomez-Romero, P., Jameson, G. B. & Baker, L. C. W. Crystal structures of α-$[Co^{II}W_{12}O_{40}]^{6-}$ and its heteropoly blue $2e^-$ reduction product, α-$[Co^{II}W_{12}O_{40}]^{8-}$. Structural, electronic, and chemical consequences of electron delocalization in a multiatom mixed-valence system. *J. Am. Chem. Soc.* **113**, 5658–5663 (1991).

73 Yu, H.-H. *et al.* Hydrothermal synthesis and structural characterization of the first mixed molybdenum-tungsten capped-keggin polyoxometal complex: $\{[Co(dien)]_4[(As^{V}O_4)Mo^{V}_8W^{VI}_4O_{33}(\mu_2\text{-}OH)_3]\}\cdot 2H_2O$. *Dalton Trans.* **33**, 195–197 (2008).

74 Li, C., Sun, M., Xu, L., Wang, Y. & Huang, J. The first heteropoly blue-embedded metal–organic framework: crystal structure, magnetic property and proton conductivity. *CrystEngComm* **18**, 596–600 (2016).

75 Wang, Y., Li, F., Xu, L., Jiang, N. & Liu, X. Multidimensional crystal frameworks based on heteropoly blue building block of $[SiW_{10}Mo^{V}_2O_{40}]^{6-}$: synthesis, structures and magnetic properties. *Dalton Trans.* **42**, 5839–47 (2013).

76 Wang, Y. *et al.* Multidimensional frameworks constructed from Keggin-type heteropoly blue of molybdenum–tungsten cluster. *CrystEngComm* **13**, 410 (2011).

77 Liu, C.-M., Zhang, D.-Q. & Zhu, D.-B. One- and two-dimensional coordination polymers constructed from bicapped keggin mixed molybdenum-vanadium heteropolyoxoanions and polynuclear copper(I) clusters bridged by asymmetrical bipyridine (2,4′-bipy and 2,3′-bipy) ligands. *Cryst. Growth Des.*, **6**, 524–529 (2006).

78 Chen, Q. & Hill, C. L. A bivanadyl capped, highly reduced Keggin polyanion, $[PMo^{V}_6Mo^{VI}_6O_{40}(V^{IV}O)_2]^{5-}$. *Inorg. Chem.* **35**, 2403–2405 (1996).

79 Dai, L. *et al.* A novel two-dimensional mixed molybdenum-vanadium polyoxometalate: Synthesis, magnetic property and characterization of {Mathematical expression}. *J. Mol. Struct.* **829**, 74–79 (2007).

80 Gu, X. *et al.* Target syntheses of saturated Keggin polyoxometalate-based extended solids. *Inorganica Chim. Acta* **358**, 3701–3710 (2005).

81 Shi, Z., Peng, J., Gómez-García, C. J., Benmansour, S. & Gu, X. Influence of metal ions on the structures of Keggin polyoxometalate-based solids: Hydrothermal syntheses, crystal structures and magnetic properties. *J. Solid State Chem.* **179**, 253–265 (2006).

82 Sha, J. *et al.* Target syntheses of two new bivanadyl capped Keggin polyoxometalate derivatives. *J. Clust. Sci.* **19**, 499–509 (2008).

83 Sha, J. *et al.* Asymmetrical polar modification of a bivanadium-capped Keggin POM by multiple Cu − N coordination polymeric

chains. *Inorg. Chem.* **46**, 11183–11189 (2007).
84 Cevik, S., Alkan, Z., Poyraz, M., Sari, M. & Buyukgungor, O. Hydrothermal synthesis and characterization of $(N(C_2H_5)_4)_4[VMo_{12}V_2O_{44}]$. *Cryst. Res. Technol.* **42**, 955–960 (2007).
85 Yu, Y. *et al.* Two novel zipper-like compounds of the usual and bivanadyl capped Keggin clusters connected by propeller-shaped complexes. *New J. Chem.* **38**, 1271–1276 (2014).
86 Meng, J.-X., Lu, Y., Li, Y.-G., Fu, H. & Wang, E.-B. Controllable self-assembly of four new metal–organic frameworks based on different phosphomolybdate clusters by altering the molar ratio of H_3PO_4 and Na_2MoO_4. *CrystEngComm* **13**, 2479–2486 (2011).
87 Ding, Y., Meng, J.-X., Chen, W.-L. & Wang, E.-B. Controllable assembly of four new POM-based supramolecular compounds by altering the POM secondary building units from pseudo-Keggin to classical Keggin. *CrystEngComm* **13**, 2687–2692 (2011).
88 Li, F. Y. *et al.* A novel cobalt(II) complex with polyoxometalate-based ligand by virtue of coexistence of both a capped-Keggin anion and a neutral unit. *J. Coord. Chem.* **58**, 1751–1758 (2005).
89 Shi, S. *et al.* 0D and 1D dimensional structures based on the combination of polyoxometalates, transition metal coordination complexes and organic amines. *CrystEngComm* **12**, 2122–2128 (2010).
90 Lu, Y., Li, Y. G., Ma, Y., Wang, E. B. & Xu, X. X. Hydrothermal synthesis and crystal structure of two new modified polyoxometalates based on $PMo_8V_6O_{42}$ clusters. *Transit. Met. Chem.* **31**, 708–713 (2006).
91 Lu, Y., Wang, E., Guo, Y., Xu, X. & Xu, L. Hydrothermal synthesis and crystal structure of a hybrid material based on $[Cu_4(bpy)_4(H_2O)_2(PO_4)_2]^{2+}$ and an α-Keggin polyoxoanion. *J. Mol. Struct.* **737**, 183–187 (2005).
92 Yao, S., Zhang, Z., Li, Y. & Wang, E. Two dumbbell-like polyoxometalates constructed from capped molybdovanadate and transition metal complexes. *Inorganica Chim. Acta* **363**, 2131–2136 (2010).
93 Müller, A., Koop, M., Schiffels, P. & Bögge, H. $[\{Mo^{VI}_8V^{IV}_4O_{36}(V^VO_4)(V^{IV}O)_2\}_n]^{7n-}$: capped α -Keggin fragments linked to a chain. *Chem. Commun*. **0**, 1715–1716 (1997).
94 Lan, Q., Zhang, Z.-M., Li, Y.-G., Lu, Y. & Wang, E.-B. Synthesis of a poly-pendant 1-D chain based on 'trans-vanadium' bicapped, Keggin-type vanadtungstate and its photocatalytic properties. *Dalton Trans.* **43**, 16265–9 (2014).
95 Zhang, Y. *et al.* Four polyoxonibate-based inorganic− organic hybrids ass embly from bicapped heteropolyoxonibate with e ff ective antitumor Activity. *Cryst. Growth Des.* **40**, 110–116 (2014).
96 Guo, G., Xu, Y., Cao, J. & Hu, C. An unprecedented vanadoniobate cluster with 'trans-vanadium' bicapped Keggin-type $\{VNb_{12}O_{40}(VO)_2\}$. *Chem. Commun.* **47**, 9411–9413 (2011).
97 Dolbecq, A., Cadot, E., Eisner, D. & Secheresse, F. Hydrothermal syntheses: A route to the stepwise condensation of reduced Keggin polyanions. From reduced beta-$[H_mSiMo_{12}O_{40}]^{n-}$ monomers to bicapped dimerized $[Si_2Mo_{28}O_{84}(H_2O)_2]^{6-}$ anions. *Inorg. Chem.* **38**, 4217–4223 (1999).
98 Han, Z.-G. *et al.* An Unusual Metallic Oxygen Cluster Consisting of a $\{AlMo_{12}O_{40}(MoO_2)\}$. *Inorg. Chem.* **53,** 670–672 (2014).
99 Mei, H., Yan, D., Chen, Q., Xu, Y. & Sun, Q. Hydrothermal synthesis, structure characterization and catalytic property of a new 1-D chain built on bi-capped Keggin type mix-valence molybdenum compound: $(NH_4)[Mo^{VI}_6Mo^V_6O_{36}(As^VO_4)Mo^V(Mo^VO)]$. *Inorg. Chim. Acta* **363**, 2265–2268 (2010).
100 Zhang, Q. B. *et al.* Synthesis and characterization of the first polyoxometalate possessing bicapped by antimony α-Keggin structure $(C_2N_2H_9)_2[(PMo^V_5Mo^{VI}_7Sb^{III}_2O_{40}]\cdot 2H_2O$. *Inorg. Chem. Commun.* **9**, 544–547 (2006).
101 Shi, S.-Y. *et al.* First examples of extended structures based on $\{PMo_{12}Sb_{2\ 40}\}$ polyoxoanions. *Dalt. Trans.* **39**, 1389–1394 (2010).
102 Liu, C.-M., Zhang, D.-Q., Xu, C.-Y. & Zhu, D.-B. Two novel windmill-like tetrasupporting heteropolyoxometalates: $[Mo^{VI}_7Mo^VV^{IV}_8O_{40}(PO_4)][M(phen)_2(OH)]_2[M(phen)_2(OEt)]_2$ (M = Co, Ni). *Solid State Sci.* **6,** 689–696 (2004).
103 Xu, Y., Zhu, H., Cai, H. & You, X. $[Mo^V_2Mo^{VI}_6V^{IV}_8O_{40}(PO_4)]^{5-}$: the first polyanion with a tetra-capped Keggin structure. *Chem. Commun.* **40,** 787–788 (1999).
104 Liu, C. M. *et al.* Spin glass behaviour in a 1D mixed molybdenum-vanadium heteropolyoxometalate-bridged coordination polymer. *Eur. J. Inorg. Chem.* 4774–4779 (2004).
105 Xu, Y., Zhu, H., Cai, H. & You, X. $[Mo^V_2Mo^{VI}_6V^{IV}_8O_{40}(PO_4)]^{5-}$: the first polyanion with a tetra-capped Keggin structure. *Chem. Commun*. **0**, 787–788 (1999).
106 Liu, C. M., Zhang, D. Q., Xiong, M. & Zhu, D. B. A novel two-dimensional mixed molybdenum-vanadium polyoxometalate with two types of cobalt(II) complex fragments as bridges. *Chem. Commun.* **853**, 1416–1417 (2002).
107 Liu, Y. B. *et al.* Hydrothermal synthesis and characterization of three one-dimensional chain materials formed by reduced tetra-capped Keggin polyoxoanions and $[M(en)_2]^{2+}$ (M = Cu, Co and Ni) cations. *J. Mol. Struct.* **825**, 45–52 (2006).
108 Sun, Y. H. *et al.* Hydrothermal synthesis and crystal structural characterization of two new modified polyoxometalates constructed of positive and negative metal-oxo cluster ions. *J. Mol. Struct.* **740,** 193–201 (2005).
109 Liu, C.-M., Zhang, D.-Q. & Zhu, D.-B. 3D Supramolecular array assembled by cross-like arrangement of 1d sandwich mixed molybdenum–vanadium polyoxometalate bridged coordination polymer chains: hydrothermal synthesis and crystal structure of $\{[Mo^{VI}_5Mo^V_3V^{IV}_8O_{40}(PO_4)][Ni(en)_2]\}[Ni(en)_2]_2\cdot 4H_2O$. *Cryst. Growth Des.* **5**, 1639–1642 (2005).
110 Sun, Y.-H. *et al.* A new mixed molybdenum–vanadium polyoxometalate double-supporting transition metal complex: $\{[Co(phen)_2]_2\text{-}C_2O_4\}\{H_2PO_{44}[Co(phen)_2(H_2O)]_2\}$. *J. Coord. Chem.* **58**, 1561–1571 (2005).
111 Cui, X.B. & Yang, G. Y. $[\{(H_2O)Ni(enMe)_2Mo^V_4Mo^{VI}_4V^{IV}_8(V^VO_4)O_{40}\}_2\{Ni(enMe)_2\}][Ni(enMe)_2]_4\cdot 8H_2O$: The First dimer of polyoxometalates linked through coordination fragment. *Chem. Lett.* **8**, 40–41 (2002).
112 Li, F. Y. *et al.* Arsenicum-centered molybdenum-vanadium polyoxometalates bearing transition metal complexes: Hydrothermal syntheses, crystal structures and magnetic properties. *J. Mol. Struct.* **753**, 61–67 (2005).
113 Long, D. L., Kögerler, P. & Cronin, L. Old clusters with new tricks: Engineering S···S interactions and novel physical properties in

sulfite-based Dawson clusters. *Angew. Chem. Int. Ed.* **43**, 1817–1820 (2004).
114 Cooper, J. B., Way, D. M., Bond, M. & Wedd, G. A green heteropoly blue - isolation of a stable, odd oxidation level in a dawson molybdate anion $[S_2Mo_{18}O_{62}]^{5-}$. *Inorg. Chem.* **32**, 2416–2420 (1993).
115 Cao, G. *et al.* Organic-inorganic heteropoly blue based on Dawson-type molybdosulfate and organic dye and its characterization and application in electrocatalysis. *Electrochim. Acta* **106**, 465–471 (2013).
116 Way, D. M., Bond, A. M. & Wedd, A. G. Multielectron reduction of α-$[S_2Mo_{18}O_{62}]^{4-}$ in aprotic and protic media: voltammetric studies. *Inorg. Chem.* **36**, 2826–2833 (1997).
117 Neier, R., Trojanowski, C. & Mattes, R. Reduced polyoxomolybdates with the keggin and dawson structures - preparation and crystal-structures of 2-electron reduced $[K(18\text{-crown-6})]_2[N(Pph_3)_2]_2[HPMo_{12}O_{40}]\cdot 8MeCN\cdot$18-crown-6 and 4-electron reduced $[NBu^n_4]_5[H_3S_2Mo_{18}O_{62}]\cdot 4MeCN$ (1 8-crown-6 = I ,4,7,10,13,16-hexaoxacyclooctadecane). *J. Chem. Soc. Trans.* 2521–2528 (1995).
118 Zhang, H. *et al.* PH and ligand dependent assembly of well-dawson arsenomolybdate capped architectures. *Inorg. Chem.* **53**, 12337–12347 (2014).
119 Fay, N. *et al.* Structural, electrochemical, and spectroscopic characterization of a redox pair of sulfite-based polyoxotungstates: α-$[W_{18}O_{54}(SO_3)_2]^{4-}$ and α-$[W_{18}O_{54}(SO_3)_2]^{5-}$. *Inorg. Chem.* **46**, 3502–10 (2007).
120 Zhu, S. *et al.* Synthesis and crystal structure determination of a novel a-Dawson mixed-valence octadecatungstoperchlorate. *J. Chem. Soc., Dalt. Trans.* 3633–3634 (1993).
121 Sun, W. *et al*. A new 3D framework based on reduced Wells-Dawson arsenotungstates as eight-connected linkages. *RSC Adv.* **4**, 24755–24761 (2014).
122 Liu, H *et al*. The mixed-valence tungstomolybdodiphosphates : Photosynthesis , characterization and studies on the added "blue" electron. *Indian J. Chem.* 2–7 (1999).
123 Contant, R. *et al.* Synthesis, characterization and electrochemistry of complexes derived from $[(1),2,3\text{-}P_2Mo_2W_{15}O_{61}]^{10-}$ and first transition metal ions. *Eur. J. Inorg. Chem.* **62**, 567–574 (2000).
124 Keita, B. *et al.* Reactions of V-substituted polyoxometalates with L-cysteine. *J. Clust. Sci.* **17**, 221–233 (2006).
125 Keita, B., Mbomekalle, I. M., Nadjo, L. & Haut, C. Tuning the formal potentials of new V^{IV}-substituted Dawson-type polyoxometalates for facile synthesis of metal nanoparticles. *Electrochem. Commun.* **6**, 978–983 (2004).
126 Miras, H. N. *et al.* Solution identification and solid state characterisation of a heterometallic polyoxometalate $\{Mo_{11}V_7\}$: $[Mo^{VI}_{11}V^{V}_{5}V^{IV}_{2}O_{52}(\mu_9\text{-}SO_3)]^{7-}$. *Chem. Commun.* **52**, 4703–4705 (2008).
127 Zhang, X., Wu, H. & Zhang, F. The three-electron heteropoly blue $[P_6Mo_{18}O_{73}]^{11-}$ with a basket- shaped skeleton. *Chem. Commun.*, 2046–2047 (2004).
128 Zhang, F.-Q., Zhang, X.-M., Fang, R.-Q. & Wu, H.-S. $P_6Mo_{18}O_{73}$ heteropolyanion and its four-copper complex: theoretical and experimental investigation. *Dalton Trans.* **39**, 8256–8260 (2010).
129 Yu, K. *et al.* A Basket-Like $[Sr\subset P_6Mo^{V}_{4}Mo^{VI}_{14}O_{73}]^{10-}$ polyoxoanion modified with $\{Cu(phen)(H_2O)_x\}$ (x = 1–3) fragments: synthesis, structure, magnetic, and electrochemical properties. *Eur. J. Inorg. Chem.* **2007**, 5662–5669 (2007).
130 Zhang, H. *et al.* Organic–Inorganic Hybrid Materials Based on Basket-like $\{Ca\subset P_6Mo_{18}O_{73}\}$ Cages. *Inorg. Chem.* **54**, 6744–6757 (2015).
131 Yu, K. *et al.* High-efficiency photo- and electro-catalytic material based on a basket-like $\{Sr\subset P_6Mo_{18}O_{73}\}$ cage. *RSC Adv.* **5**, 59630–59637 (2015).
132 Zhang, H. *et al.* Assembly of a basket-like $\{Sr\subset P_6Mo_{18}O_{73}\}$ cage from 0D dimmer to 2D network and its photo-/electro-catalytic properties. *Dalton Trans.* **44**, 12839–12851 (2015).
133 Zhang, H. *et al.* 1,4-Bis(imidazole)butane ligand and strontium(ii) directed 1-D chains based on basket-type molybdophosphates and transition metal (TM) linkers. *CrystEngComm* **17**, 6110–6119 (2015).
134 Chen, Z. Y. *et al.* Nonclassical Phosphomolybdates with Different Degrees of Reduction: Syntheses and Structural and Photo/Electrocatalytic Properties. *Inorg. Chem.* **55**, 8309–8320 (2016).
135 Yu, K. *et al.* Supramolecular assembly based on Keggin cluster and basketlike cage. *Inorg. Chem. Commun.* **14**, 1846–1849 (2011).
136 Yu, K. *et al.* A Basket-Like $[Sr\subset P_6Mo^{V}_{4}Mo^{VI}_{14}O_{73}]^{10-}$ Polyoxoanion Modified with {Cu(phen)(H2O)x} (x = 1–3) Fragments: Synthesis, Structure, Magnetic, and Electrochemical Properties. *Eur. J. Inorg. Chem.* **2007**, 5662–5669 (2007).
137 Deng, W., Zhang, Q. & Wang, Y. Polyoxometalates as efficient catalysts for transformations of cellulose into platform chemicals. *Dalt. Trans.* **41**, 9817 (2012).
138 Wang, W. et al. The basket-type dimer layers based on tetra-electron reduced heteropoly blue directed by copper/nickel and strontium linkers. *New J. Chem.* **41**, 2687–2694 (2017).
139 Nakamura, I. *et al.* Investigating the Formation of 'Molybdenum Blues' with Gel Electrophoresis and Mass Spectrometry. *J. Am. Chem. Soc.* **137**, 6524–6530 (2015).
140 Fujibayashi, M., Song, Y.-F., Cronin, L. & Tsunashima, R. Exploring the solvent mediated assembly and redox activity of a POM–organic hybrid $[Na(SO_3)_2(PhPO_3)_4Mo^{V}_{4}Mo^{VI}_{14}O_{49}]^{5-}$. *New J. Chem.* **40**, 8488–8492 (2016).
141 Dumas, E., Debiemme-Chouvy, C. & Sevov, S. C. A reduced polyoxomolybdenum borophosphate anion related to the Wells-Dawson clusters. *J. Am. Chem. Soc.* **124**, 908–909 (2002).
142 Fujibayashi, M., Song, Y.-F., Cronin, L. & Tsunashima, R. Exploring the solvent mediated assembly and redox activity of a POM–organic hybrid $[Na(SO_3)_2(PhPO_3)_4Mo^{V}_{4}Mo^{VI}_{14}O_{49}]^{5-}$. *New J. Chem.* **40**, 8488–8492 (2016).
143 Khan, M. I., Tabussum, S., Doedens, R. J., Golub, V. O. & O'Connor, C. J. Functionalized metal oxide clusters: synthesis, characterization, crystal structures, and magnetic properties of a novel series of fully reduced heteropolyoxovanadium cationic clusters decorated with organic ligands – $[MV^{IV}_{6}O_6\{(OCH_2CH_2)_2N(CH_2CH_2OH)\}_6]X$ (M = Li, X = Cl·LiCl; M = Na, X = Cl·H_2O; M = Mg,

X = 2Br·H_2O; M = Mn, Fe, X = 2Cl; M = Co, Ni, X = 2Cl·H_2O). *Inorg. Chem.*, **43**, 5850–5859 (2004).

144 Khan, M. I. *et al.* Organo-functionalized metal-oxide clusters: synthesis and characterization of the reduced cationic species $[NaV^{IV}_6O_6\{(OCH_2CH_2)_2NH\}_6]^+$. *Dalton Trans.* **43**, 16509–16514 (2014).

145 Khan, M. I., Tabussum, S., & Doedens, R. J. A novel cationic heteropolyoxovanadium(IV) cluster functionalized with organic ligands: synthesis and characterization of the fully reduced species $[Mn^{II}V^{IV}_6O_6\{(OCH_2CH_2)_2N(CH_2CH_2OH)\}_6]Cl_2$. *Chem. Commun.*, 532–533 (2004).

146 Zhang, Y.-T. *et al.* Synthesis, structures, and magnetic properties of metal–organic polyhedra based on unprecedented $\{V_7\}$ isopolyoxometalate clusters. *Dalt. Trans.* 14898–14901 (2016).

147 Zhang, Y.-T. *et al.* Anderson-like alkoxo-polyoxovanadate clusters serving as unprecedented second building units to construct metal–organic polyhedra. *Chem. Commun.* **47**, 3909–3913 (2016).

148 Mak, W. & Huangb, K. A Hexanuclear oxovanadium(IV) anionic aggregate containing μ_2- and μ_6-carbonato groups: synthesis and structural characterization of $(NH_4)_5[(VO)_6(CO)_4(OH)_9]\cdot 10H_2O$. *J. Chem. Soc., Chem. Commun.*, 1597–1598 (1986).

149 Li, H., Swenson, L., Doedens, R. J. & Khan, M. I. An organo-functionalized metal–oxide cluster, $[V^{IV}_6O_6\ \{(OCH_2CH_2)_2N(CH_2CH_2OH)\}_6]$, with Anderson-like structure. *Dalt. Trans.* **45**, 16511–16518 (2016).

150 Haushalter, R. C. & Lai, F. W. Synthesis of a new one-dimensional sodium molybdenum phosphate polymer: structure of $[(H_3O)_2NaMo_6P_4O_{24}(OH)_7]^{2-}$. *Inorg. Chem.* **28**, 2904–2905 (1989).

151 Haushalter, R. C. & Lai, F. W. $[Et_4N]_6[Na_{14}Mo_{24}P_{17}O_{97}(OH)_{31}]\cdot xH_2O$: a hollow cluster filled with 12 Na^+ ions and a H_3PO_4 molecule. *Angew. Chem. Int. Ed.* **28**, 743–746 (1989).

152 Guesdon, A., Borel, M. M., Leclaire, A. & Raveau, B. Two new closely related Mo^V hydroxymonophosphates built up of $Cd[Mo_6P_4O_{25}(OH)_6]_2$ and $Cd[Mo_6P_4O_{26}(OH)_5]_2$ clusters. *Chem. Eur. J.* **3**, 1797–1800 (1997).

153 Dolbecq, A., Cadot, E. & Sécheresse, F. $[Mo_9S_8O_{12}(OH)_8(H_2O)_2]^{2-}$: a novel polyoxothiomolybdate with a Mo^{VI} octahedron encapsulated in a reduced Mo^V cyclic octanuclear core. *Chem. Commun*., 2293–2294 (1998).

154 Cadot, E., Dolbecq, A., Salignac, B. & Sécheresse, F. Self-Condensation of $[Mo^V_2O_2S_2]^{2+}$ with phosphate or arsenate ions by acid–base processes in aqueous solution: syntheses, crystal structures, and reactivity of $[(HXO_4)_4Mo_6S_6O_6(OH)_3]^{5-}$, X=P, As. *Chem. Eur. J.*, **5**, 2396–2403 (1999).

155 Chang, W.-J., Jiang, Y.-C., Wang, S.-L. & Lii, K.-H. Hydrothermal synthesis of a three-dimensional organic-inorganic hybrid network formed by poly(oxomolybdophosphate) anions and nickel coordination cations. *Inorganic Chemistry*, **45**, 6586–6588 (2006).

156 Mundit, L. A. & Haushalter, R. C. Hydrothermal synthesis of a layered zinc molybdenum phosphate with octahedral and tetrahedral zinc : structure of $(TMA)_2(H_3O)_2[Zn_3Mo_{12}O_{30}(HPO_4)_2(H_2PO_4)_6]\cdot 11.5\ H_2O$. , *Inorg. Chem.* **31**, 3050–3053 (1992).

157 Mundit, L. A. & Haushalter, R. C. Hydrothermal synthesis, structure, and sorption properties of the new microporous ferric molybdenum phosphates $[(CH_3)_4N]_2(NH_4)_2[Fe_2Mo_{12}O_{30}(H_2PO_4)_6(HPO_4)_2]\cdot nH_2O$ and $[(CH_3)_4N]_2Na_4[Fe_3Mo_{12}O_{30}(H_xPO_4)_8]\cdot nH_2O$. *Inorg. Chem.* **32**, 1579–1586 (1993).

158 Cao, G., Haushalter, R. C. & Strohmaier, K. G. A novel polyoxo molybdenum(V) organophosphonate anion having a sandwich structure: synthesis and crystal structure of $[N(C_2H_5)_4]_2Na_3(H_3O)_4\{Na[Mo_6O_{15}(O_3PC_6H_5)(HO_3PC_6H_5)_3]_2\}\cdot{\sim}H_2O$. *Inorg. Chem.* **32**, 127–128 (1993).

159 Khan, K. M., Chen, M. I., & Zubieta, J. Oxomolybdenum (V) polyanion clusters. Hydrothermal syntheses and structures of $(NH_4)_5Na_4\{Na[Mo_6O_{12}(OH)_3(O_3PC_6H_5)_4)]_2\}\cdot 6H_2O$ and $(C_6H_5CH_2NMe_3)_4K_4\{K_2[Mo_6O_{12}(OH)_3(O_3PC_6H_5)_4]_2\}\cdot 10H_2O$ and their relationship to the binuclear $(Et_4N)[Mo_2O_4Cl_3(H_2O)_3]\cdot 5H_2O$. *Inorg. Chim. Acta* **235**, 135–145 (1995).

160 Streb, C., Long, D.-L. & Cronin, L. Engineering porosity in a chiral heteropolyoxometalate-based framework: the supramolecular effect of benzenetricarboxylic acid. *Chem. Commun*., 471–473 (2007).

161 Xu, L. *et al.* A manganese molybdenum phosphate with a tunnel : hydrothermalsynthesis, structure and catalytic properties of $(NH_3CH_2CH_2NH_3)_{10}(H_3O)_3(H_5O_2)Na_2[MnMo_{12}O_{24}(OH)_6(PO_4)_4(PO_3OH)_4][MnMo_{12}O_{24}(OH)_6(PO_4)_6(PO_3OH)_2]\cdot 9H_2O$. *New J. Chem.* **23**, 1041–1044 (1999).

162 Zhang, H. *et al.* The highest connected pure inorganic 3D framework assembled by $\{P_4Mo_6\}$ cluster and alkali metal potassium. *RSCAdv.* **5**, 3552–3559 (2015).

163 Wang, W., Han, Z., Wang, X., Zhao, C. & Yu, H. Polyanionic clusters $[M(P_4Mo_6)_2]$ (M = Ni, Cd) as effective molecular catalysts for the electron-transfer reaction of ferricyanide to ferrocyanide. *Inorg. Chem.* **55**, 6435−6442 (2016).

164 Manos, M. J., Keramidas, A. D., Woollins, J. D., Slawin, A. M. Z. & Kabanos, T. A. The first polyoxomolybdenum carbonate compound: Synthesis and crystal structure of $(NH_4)_5[(Mo_2^VO_4)_3(\mu 6\text{-}CO_3)(\mu\text{-}CO_3)_3(\mu\text{-}OH)_3]\cdot 0.5\ CH_3OH$ 1. *J. Chem. Soc. Trans.* **3** 3419–3420 (2001).

165 Peloux, C. *et al.* A new family of layered molybdenum (V) cobalto-phosphates built up of $[H_{14}(Mo_{16}O_{32})Co_{16}(PO_4)_{24}(H_2O)_{20}]^{10-}$ wheels. *Angew. Chem. Int. Ed.* **40**, 2455−2457 (2001).

166 Peloux, C. *et al.* A new two-dimensional molybdenum(V) nickel phosphate built up of $[H_{18}(Mo_{16}O_{32})Ni_{16}(PO_4)_{26}(OH)_6(H_2O)_8]^{10-}$ wheels. *Inorg. Chem.* **41**, 7100− 7104 (2002).

167 Zhang, Y.-N., Zhou, B.-B., Li, Y.-G., Sua, Z.-H & Zhao, Z.-F. A new molybdenum(V) nickel phosphate based on divacant $[H_{30}(MoV_{16}O_{32})Ni_{14}(PO_4)_{26}O_2(OH)_4(H_2O)_8]^{12-}$ wheel. *Dalton Trans.* 9446–9451 (2009).

168 Yu, K., Zhou, B. Bin, Yu, Y., Su, Z. H. & Yang, G. Y. A new organic-inorganic hybrid layered molybdenum(V) cobalt phosphate constructed from $[H_{24}(Mo_{16}O_{32})Co_{16}(PO_4)_{24}(OH)_4(C_5H_4N)_2(H_2O)_6]^{4-}$ wheels and 4,4′-bipyridine linkers. *Inorg. Chem.* **50**, 1862–1867 (2011).