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SUPPLEMENTARY INFORMATION

Synthesis, structures and applications of electron-rich polyoxometalates

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

Archetype	Formula	Number of blue e^-	Educts	Synthetic conditions	Characterization methods	Application	Ref.
			Isopolymolybdates				
Lindqvist	$(NBu_4)_3[Mo^{V}Mo^{VI}_5O_{19}]$	1	$(N^nBu_4)_2[Mo^{VI}_6O_{19}]$	electrolysis in DMF with NBu_4BF_4 at −1.1 V	EA, IR, EPR, polarography	nr	1–3
Hepta-molybdate	$[N^iPrH_3]_6[Mo^{VI}O_5(OH)Mo^{VI}_6O_{18}]$	1	$(N^iPrH_3)_6[Mo^{VI}_7O_{24}]$	UV-irradiation of a single crystal $(NPrH_3)_6[Mo^{VI}_7O_{24}]$ ($\lambda \geq 313$ nm)	EPR, SC-XRD	nr	4,5
χ-Octamolybdate	$(NBu_4)_6[Mo^{VI}_6O_{17}(NC_6H_{11})_2][Mo^{V}_4Mo^{VI}_4O_{24}]$	4	α-$(N^nBu_4)_4[Mo^{VI}_8O_{26}]$, TETA, DCC	reflux in dry MeCN	EA, IR, ESI-MS, UV-vis, CV, SC-XRD	nr	6
Keggin derivatives	$[NMe_3H]_6[H_2Mo^{V}_{12}O_{28}(OH)_{12}(Mo^{VI}O_3)_4]$	12	$(N^iPrH_3)_6[Mo^{VI}_7O_{24}]$	prolonged photolysis in aqueous solution, pH 5–6, 4 d	EA, IR, ESI-MS, CV, ^{95}Mo NMR, SC-XRD	anti-tumor activity [7, 8]	9
	$[NMe_2H_2]_6[H_2Mo^{V}_{12}O_{28}(OH)_{12}(Mo^{VI}O_3)_4]$	12	$Mo^{VI}O_3$, $Na_2[Mo^{VI}O_4]$, $C(CH_2OH)_4$, NEt_4CI, Me_3NH, H_2O	HT 160 °C, 3 d	EA, IR, SC-XRD	nr	10
	$H_2py_3[H_4Mo^{IV}_6Mo^{VI}_7O_{36}py_6]\cdot 2H_2O$	12	$[Mo^{IV}_3O_4(H_2O)_9]^{4+}$, H_3nta, pyridine	HT 120 °C, 3 d, pH = 3	EA, IR, SC-XRD	nr	11
"Shrink-wrapped"	$(C_6H_{13}N_4)_{10}[H_2Mo^{V}_4Mo^{VI}_{12}O_{52}]\cdot 34H_2O$	4	$Na_2[Mo^{VI}O_4]$, $Na_2S_2O_4$, HCl, HMTAH	pH 4–4.5	EA, IR, UV-vis, SC-XRD, BVS, DFT, magnetometry	nr	12
Deca-molybdate	$(N^nBu_4)[Mo^{V}_2Mo^{VI}_7O_{25}(OMe)_6(Mo^{II}NO)]$	2	$(N^nBu_4)_2[Mo^{VI}_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}]$, VCl_3	reflux in MeOH, 4 h	EA, IR, SC-XRD, electrochemistry, magnetometry, Hückel calc.	nr	13
	$(N^nBu_4)_2[Mo^{V}_4Mo^{VI}_5O_{24}(OMe)_7(Mo^{II}NO)]$	4	$(N^nBu_4)_2[Mo^{VI}_6O_{18}(NO)]$, $N_2H_4\cdot 2HCl$	reflux in 1:1 mixture of MeOH and MeCN, 7 h	EA, IR, SC-XRD, electrochemistry, magnetometry, Hückel calc.	nr	14
			Isopolytungstates				
Lindqvist	$NEt_4[W^{V}W^{VI}_5O_{19}]\cdot 0.5H_2O$	1	$Na_2[W^{VI}O_4]$, $Mo^{VI}O_3$, Mo^0, $NEt_4CI\cdot H_2O$, H_2O	HT 160 °C, 3,5 d	EA, IR, TGA, SC-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	$Na_2[W^{VI}O_4]$, V^0, $H_2N(CH_2)_2NH_2\cdot 2HCl$, H_2O	HT 160 °C, 3,75 d	EA, IR, TGA, SC-XRD, magnetometry	nr	14
	$[Fe^{III}(C_5H_5)_2]_3[W^{V}W^{VI}_5O_{19}]$	1	$Na_2[W^{VI}O_4]$, NaOAc, HOAc, $[Fe^{II}(C_5H_5)_2]$, THF, HCl	85 °C, 1 d	EA, IR, SC-XRD, magnetometry	nr	15

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Metatungstate	$[H_2W^{V}{}_nW^{VI}{}_{10}O_{40}]^{(6+n)-}$ (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]
	$Rb_4H_8[H_2W^{IV}{}_3W^{VI}{}_9O_{40}]\cdot 18H_2O$	6	$Na_6[H_2W^{VI}{}_{12}O_{40}]$, RbCl, NaOAc	electrolysis on a Hg cathode at –0.53 V vs. SCE in 0.5 M HCl	EA, SC-XRD	nr	[18]
	$(NH_4)_4H_8[H_2W^{IV}{}_3W^{VI}{}_9O_{40}]$	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]
	$(NH_4)_4H_8[H_2W^{IV}{}_3W^{VI}{}_9O_{40}]$	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 H_2 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]
Decatungstate	$[H_5O_2][NH_2{}^iPr_2]_4[W^{V}W^{VI}{}_9O_{32}]\cdot 4H_2O$ + $[H_5O_2]_2[NH_2{}^iPr_2]_4[W^{V}{}_2W^{VI}{}_8O_{32}]\cdot 4H_2O$	1 – 2	$(N^iPr_2H_2)_4[W^{VI}{}_{10}O_{32}]$	UV photolysis (λ > 310 nm)	EA, IR, ^{183}W NMR, EPR, SC-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	$C_6H_{16}N_4[W^{VI}{}_{10}O_{32}]\cdot 2MeCN$	UV photolysis (λ > 300 nm), 20 h	EA, SC-XRD	nr	[25]
	$Na_4[HW^{V}W^{VI}{}_9O_{32}] + 4\ Na_4[H_2W^{V}{}_2W^{VI}{}_8O_{32}]$	1 – 2	$Na_2[W^{VI}O_4]$, $HClO_4$, MeCN	1) 80 °C, pH = 1; 2) UV photolysis (λ > 300 nm), 20 h	EA, SC-XRD	nr	[25]
	$[N^nBu_4]_5[W^{V}W^{VI}{}_9O_{32}]$	1	$[N^nBu_4]_4[W^{VI}{}_{10}O_{32}]$	electrolysis in DMF at –1.3 V or UV photolysis	EA, IR, UV-vis, EPR	nr	[26]
	$[N^nBu_4]_6[W^{V}{}_2W^{VI}{}_9O_{32}]$	2	$[N^nBu_4]_4[W^{VI}{}_{10}O_{32}]$	electrolysis in MeCN 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, SC-XRD, magnetometry	nr	[28]
	$[V^{IV}{}_3V^{V}{}_3O_8(OMe)_{11}]$	3	1) $V^{V}O(O^tBu)_3$, MeOH; 2) $V^{V}O(OMe)_3$, MeOH, ^{t}BuNOH, I_2	HT 125 °C, 24 h	EA, IR, UV-vis, CV, SC-XRD, BVS	nr	[29]
	$(N^nBu_4)_2[V^{IV}{}_3V^{V}{}_3O_{10}(OH)_3((OCH_2)_3CNO_2)_2]\cdot 0.67\ CH_2Cl_2$	3	$(TBA)_2[V^{V}{}_6O_{10}(OH)_3((OCH_2)_3CNO_2)_2]$, 1,1-methylphenylhydrazine, CH_2Cl_2	RT, 5 h	EA, IR, SC-XRD	inhibition of ATPase	[31]

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	$[V^{IV}_3V^{V}_2O_6(OMe)_{12}Fe^{III}O_3SCF_3]$	3	$V^{V}O(OMe)_3$, $Fe^{II}Br_2$, PhMe, AgO_3SCF_3, MeCN	85 °C, 110 h	EA, IR, ESI-MS, CV, SC-XRD, magnetometry	nr	[32]
	$[V^{IV}_4V^{V}_2O_7(OMe)_{12}]$	4	$V^{V}O(O^{t}Bu)_3$, $N^{n}Bu_4BH_4$, MeOH	HT 125 °C, 24 h	EA, IR, CV, SC-XRD, BVS	nr	[33, 34]
	$[V^{IV}_4V^{V}_2O_7(OEt)_{12}]$	4	$V^{V}O(OEt)_3$, $N^{n}Bu_4BH_4$, EtOH	HT 125 °C, 24 h	EA, IR, CV, DCS, ESI-MS, SC-XRD, BVS	nr	[35, 36]
	$(N^{n}Bu_4)_2[V^{IV}_4V^{V}_2O_9(OH)_4\{(OCH_2)_3CMe\}_2]$	4	$(N^{n}Bu_4)_2[V^{V}_6O_{13}\{(OCH_2)_3CMe\}_2]$, $Me(Ph)NNH_2$	RT, 5 h	EA, IR, UV-vis, ^{17}O NMR, EPR, SC-XRD, electrochemistry, magnetometry	nr	[37]
	$(NMe_3H)[V^{IV}_5V^{V}O_7(OH)_3\{(OCH_2)_3CMe\}_3]$	5	$V^{III}_2O_3$, $V^{V}_2O_5$, $(HOCH_2)_3CMe$, NMe_3HCl, Et_3NHCl, H_2O	HT 210 °C, 17 h	EA, IR, SC-XRD, electrochemistry, magnetometry	nr	[38]
	cis-$Na_2[V^{IV}_6O_7(OH)_6\{(OCH_2)_3CH_2OH\}_2]\cdot 8H_2O$	6	$Na[V^{V}O_3]$, N_2H_5OH, $(HOCH_2)_3CH_2OH$, H_2O	80 °C, 7 h	EA, IR, UV-vis, CV, EPR, SC-XRD, magnetometry	nr	[28]
	$Ba[V^{IV}_6O_7(OH)_3\{(OCH_2)_3CMe\}_3]\cdot 3H_2O$	6	$V^{III}_2O_3$, $K[V^{V}O_3]$, $(HOCH_2)_3CMe$, $BaCl_2\cdot 2H_2O$, H_2O	HT 150 °C, 50 h	EA, IR, SC-XRD, electrochemistry, magnetometry	nr	[38]
	$Na_2[V^{IV}_6O_7\{(OCH_2)_3CEt\}_4]$	6	$V^{III}_2O_3$, $Na[V^{V}O_3]$, $(HOCH_2)_3CEt$, NaCl, H_2O	HT 150 °C, 21 h	EA, IR, SC-XRD, electrochemistry, magnetometry	nr	[38]
	$(N^{n}Bu_4)_2[V^{IV}_6O_7(OH)_6\{(OCH_2)_3CMe\}_2]$	6	$(N^{n}Bu_4)_2[V^{V}_6O_{13}\{(OCH_2)_3CMe\}_2]$, CH_2Cl_2, PhNHNHPh	RT, 10 h	EA, IR, UV-vis, ^{17}O NMR, EPR, SC-XRD, electrochemistry, magnetometry	nr	[37]
	(cat)$[V^{III}V^{IV}_5O_6(OMe)_8$(4-*tert*-butylcalix[4]arene – 4H)(MeOH)] (cat = NEt_4, NH_4, PyH, NEt_3H)	6	$V^{IV}OSO_4$, 4-*tert*-butylcalix[4]arene, MeOH and either NEt_4OH, NH_4OH, NEt_3 or pyridine	HT 170 °C, 3 d	EA, IR, SC-XRD, magnetometry, DFT	nr	[39]
Decavanadate	$(NH_4)_4[V^{IV}_{10}O_{16}\{(OCH_2)_3CEt\}_4]\cdot 4H_2O$	10	$V^{III}_2O_3$, $NH_4[V^{V}O_3]$, $(HOCH_2)_3CEt$, NH_4Cl, H_2O	HT 150 °C, 20 h	EA, IR, SC-XRD, electrochemistry, magnetometry	nr	[34]
	$NMe_4[V^{IV}_{10}O_{13}\{(OCH_2)_3CEt\}_5]$	10	$V^{III}_2O_3$, $V^{V}_2O_5$, $(HOCH_2)_3CEt$, NMe_4Br, NMe_4Cl, H_2O	HT 200 °C, 22 h	EA, IR, SC-XRD, electrochemistry, magnetometry	nr	[34]

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	$(NMe_3H)_2[V^{IV}_{10}O_{14}(OH)_2\{(OCH_2)CCH_2OH\}_4]\cdot 2H_2O$	10	$V^{III}_2O_3$, $V^{V}_2O_5$, $Na[V^{V}O_3]$, $(HOCH_2)_3CCH_2OH$, Et_3NHCl, H_2O	HT 150 °C, 20 h	EA, IR, CV, SC-XRD, magnetometry	nr	[40]
	$Na_2[V^{IV}_8V^{V}_2O_{16}((OCH_2)CEt)_4]$	8	$V^{III}_2O_3$, $Na[V^{V}O_3]$, NaCl, Cu_2Br, $(HOCH_2)_3CEt$, H_2O	HT 150 °C, 50 h	EA, IR, CV, SC-XRD, magnetometry	nr	[40]
	$K_2[V^{IV}_8V^{V}_2O_{16}((OCH_2)CEt)]\cdot 2H_2O$	8	$V^{III}_2O_3$, $K[V^{V}O_3]$, KCl, $MnCl_2$, $(HOCH_2)_3CEt$, H_2O	HT 150 °C, 40 h	EA, IR, CV, SC-XRD, magnetometry	nr	[40]
	$(N^nBu_4)_2[V^{IV}_8V^{V}_2O_{16}\{(OCH_2)_3CMe\}]$	8	$V^{III}_2O_3$, $V^{V}_2O_5$, $V^{IV}OSO_4$, $(HOCH_2)_3CMe$, N^nBu_4OH, H_2O	HT 150 °C, 90 h	EA, IR, SC-XRD, magnetometry	nr	[40]
"Wheel-like" decavanadate	$(N^nBu_4)_4[V^{IV}_2V^{V}_8O_{26}]\cdot H_2O$	2	$(N^nBu_4)_2[\{(\eta^3\text{-}C_4H_7)Pd\}_2V_4O_{12}]$, MeCN	reflux under N_2, 2 h	EA, SC-XRD	nr	[41]
	$(NEt_4)_4[V^{IV}_2V^{V}_8O_{26}]\cdot H_2O$	2	$V^{IV}O(acac)_2$, $Cu(acac)_2$, CH_2Cl_2, NEt_4Cl	RT, 1 h	EA, IR, EPR, TGA, SC-XRD	nr	[42, 43]
	$(N^nBu_4)_4[V^{IV}_2V^{V}_8O_{26}]\cdot 2DMF$	2	$(N^nBu_4)_4[V^{V}_4O_{12}]$, DMF, $N^tBu(CH_2CH_2OH)_2$	UV irradiation ($\lambda > 380$ nm), 90 °C, overnight	EA, IR, UV-vis, SC-XRD	nr	[44, 45]
	$(N^nBu_4)_4[V^{IV}_2V^{V}_8O_{26}]$	2	$V^{V}_2O_5$, $V^{IV}OSO_4$, N^nBu_4OH, Me_2CO, 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 – eloctrospray ionization mass spectrometry
HT – hydrothermal synthesis
IR – infrared spectroscopy
NMR – nuclear magnetic resonance
PXRD – powder X-ray diffraction
RT – room temperature
SC-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
DCC – N,N′-dicyclohexylcarbodiimide
Et – ethyl
HMTAH – hexamethylenetetramine
Me – methyl
nta – nitrilotriacetate
^{i}Pr – isopropyl
py - pyridine
TETA – triethylenetetramine

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Table S2 | **Selected details of synthesis and characterisation of reduced of non-capped Keggin type anions. The compounds in each section are presented in ascending order of reduction.**

Heteroatom X	Formula	Number of blue e^-	Educts	Synthetic conditions	Characterization methods	Application	Ref.
POMos with Keggin anions $XMo^{V}_{n}Mo^{VI}_{12-n}$							
P^{V}	$[K_2Ag_{15}(5\text{-}o\text{-tolyl-}1H\text{-tetrazole})_{10}(H_2O)_2][H(PMo^{V}Mo^{VI}_{11}O_{40})_2]$	1	$H_3[PMo^{VI}_{12}O_{40}]$, $AgNO_3$, 5-*o*-tolyl-1*H*-tetrazole, HNO_3, H_2O	HT 160 °C, 3 d, pH = 2.13	EA, IR, UV-vis, SC-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	$Na_2[Mo^{VI}O_4]$, HCl, H_3PO_4, $N_2H_5(HSO_4)$, Ni^{2+}	RT	EA, IR, SC-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, SC-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, SC-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, SC-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	$Na[V^{V}O_3]$, $Na_2[Mo^{VI}O_4]$, $Ni(OAc)_2$, phen, H_2O, H_3PO_4	HT 160 °C, 5 d, pH = 4.5	EA, IR, UV-vis, SC-XRD	nr	51
	$(N^{n}Bu_4)_3[PMo^{V}_2Mo^{VI}_{10}O_{40}\{Co(MeCN)_2\}]$	2	$(N^{n}Bu_4)_3[PMo^{VI}_{12}O_{40}]$, $CoCl_2$, MeCN, Na/Hg amalgam	12 h	EA, IR, ^{31}P NMR, CV, SC-XRD	nr	52
	$[Ni(phen)_3][PMo^{V}_3Mo^{VI}_9O_{40}\{Ni(phen)\}_2]$	3	$(NH_4)_6[Mo^{VI}_7O_{24}]$, $NiCl_2$, H_3PO_4, phen, H_2O	HT 160 °C, 7 d, pH = 3.8	EA, IR, UV-vis, EPR, SC-XRD	nr	53
	$Ca_{0.5}H_6PMo^{V}_4Mo^{VI}_8O_{40} \cdot 18H_2O$	4	$Na_2[Mo^{VI}O_4]$, H_3PO_4, HCl, $CaCl_2 \cdot 2H_2O$	electrolysis under N_2 on a Pt electrode, at –0.2 V vs. SCE	EA, SC-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, SC-XRD	nr	55
	$[Co^{II}(2,2'\text{-bipy})_3]_6(H_2\text{-}2,2'\text{-bipy})[Co^{II}(2,2'\text{-bipy})_2(PMo^{V}_4Mo^{VI}_8O_{40})]_3[Co^{II}(2,2'\text{-bipy})(PMo^{V}_4Mo^{VI}_8O_{40})] \cdot 16H_2O$	4	$Na_2[Mo^{VI}O_4]$, $Co(OAc)_2$, 2,2′-bipy, 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, SC-XRD	H_2O oxidation to generate O_2 under visible light irradiation	56
	$(N^{n}Bu_4)_3[H_4PMo^{V}_8Mo^{VI}_4O_{40}Zn_4][C_7H_6(CO_2)_2]_2$	8	$Na_2[Mo^{VI}O_4]$, Mo^0, $ZnCl_2$, H_3PO_4, $H_2C_2O_4$, $N^{n}Bu_4OH$, H_2O	HT 180 °C, 3 d, pH = 4.9	EA, IR, TGA, PXRD, SC-XRD	electrocatalyst for reduction of BrO_3^-	57, 58

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	$[H_3O][Hdma]_3[H_2phen]\{[Cr(phen)]_2[Mo^{V}_9Mo^{VI}_3O_{36}(PO_4)]\}\cdot nH_2O$ ($n \approx 1$)	9	$(NH_4)_2[Mo^{VI}O_4]$, $K_2Cr_2O_7$, H_3PO_3, phen, DMF, H_2O	HT 160 °C, 7 d	EA, IR, UV-vis, XPS, TGA, cerate oxidimetry, SC-XRD	nr	[59]
S^{VI}	α-$(N^nBu_4)_3[S^{VI}Mo^{V}Mo^{VI}_{11}O_{40}]$	1	$(Nhexyl_4)_2[SMo^{VI}_{12}O_{40}]$, CH_2Cl_2	electrolysis, at –0.1 V vs. Fc^+/Fc	EA, IR, EPR, SC-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	$Na_2[Mo^{VI}O_4]$, GeO_2, $Ni(OAc)_2$, pda, bpe, H_2O, H_2SO_4	HT 170 °C, 4 d, pH = 6.0	EA, IR, XPS, TGA, SC-XRD, magnetometry	nr	[61]
Ni^{II}	$[Mo^{V}_8Mo^{VI}_4O_{30}(\mu^2\text{-}OH)_6(Ni^{II}O_4)\{Ni^{II}(en)(H_2O)\}_4]$	8	$Mo^{VI}O_3$, $Ni(OAc)_2$, en, H_2O	HT 160 °C, 2 d	EA, SC-XRD	nr	[62]
	$[Mo^{V}_{12}O_{30}(\mu^2\text{-}OH)_{10}H_2\{Ni^{II}_4(H_2O)_{12}\}]$	12	$(NH_4)_6[Mo_7O_{24}]$, $Ni(OAc)_2$, $(N_2H_5)HSO_4$, HOAc, H_2O	65 °C, 3 d	EA, IR, SC-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	$Na_2[W^{VI}O_4]$, H_3PO_4, $Cu(NO_3)_2$, tib, EtOH, H_2O	HT 160 °C, 3 d, pH = 3.66	EA, IR, TGA, XPS, SC-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, SC-XRD, photoluminescence analysis	electrocatalyst for reduction of NO^{2-}, IO_3^- and oxidation of ascorbic acid	[65]
	$[Cu(2,2'\text{-bipy})_2]_5[PW^{V}_2W^{VI}_{10}O_{40}]\cdot 2H_2O$	2	$Na_2[W^{VI}O_4]$, NaH_2PO_4, $CuCl_2$, 2,2′-bipy, EtOH, H_2O	HT 160 °C, 6 d, pH = 5	EA, IR, SC-XRD, electrochemistry	electrocatalyst for reduction of NO^{2-}	[66]
	$Co(tib)_2[PW^{V}_3W^{VI}_9O_{38}]\cdot 5H_2O$	3	$Na_2[W^{VI}O_4]$, H_3PO_4, $Co(NO_3)_2$, tib, H_2O	HT 160 °C, 3 d, pH = 4.35	EA, IR, TGA, XPS, SC-XRD, electrochemistry	nr	[64]
	$[Ni(enMe)_2(H_2O)_2]_2[Ni(enMe)_2PW^{V}_3W^{VI}_9O_{40}]\cdot H_2O$	3	$Na_2[W^{VI}O_4]$, $NiCl_2$, enMe, H_2O, H_3PO_4	HT 180 °C, 3 d, pH = 5.0 – 5.5	EA, IR, XPS, SC-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, SC-XRD, electrochemistry	nr	[68]
	$[Na(H_2O)_2\{M^{I}(btp)_4\}(PW^{V}_4W^{VI}_8O_{39}]$ (M = Cu, Ag))	4	$Na_2[W^{VI}O_4]$, $Cu(OAc)_2$ or $AgNO_3$, bpt, H_2O, H_3PO_4	HT 160 °C, 5 d, pH = 3.5	EA, IR, TGA, SC-XRD, electrochemistry	electrocatalyst for reduction of NO^{2-}; fluorescence properties at RT	[69]
Si^{IV}	$[Ag_4(2\text{-btz})_5K(SiW^{I}W^{VI}_{11}O_{40})]\cdot 13H_2O$	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, SC-XRD	nr	[50]

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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	$Cu(OAc)_2$, $Na_2[W^{VI}O_4]$, 2,2′-bipy, EDTA, NaOH, Al_2O_3, H_2O	HT 180 °C, 3 d, pH = 5	EA, IR, EPR, TGA, SC-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 –0,13 V vs. NHE	EA, IR, CV, ^{27}Al NMR, SC-XRD	nr	[71]
Co^{II}	$K_{7.77}[Co^{II}W^{V}_2W^{VI}_{10}O_{40}]_{0.885}[Co^{II}W^{VI}_{12}O_{40}]_{0.115}\cdot 9.7H_2O$	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, SC-XRD	nr	[72]
Mixed Mo/W POMs with Keggin anions $XMo^{V}_nW^{VI}_{12-n}$							
As^{V}	$\{[Co(dien)]_4[(As^{V}O_4)Mo^{V}_8W^{VI}_4O_{33}(\mu\text{-}OH)_3]\}\cdot 2H_2O$	8	$W^{VI}O_3$, $Mo^{VI}O_3$, As_2O_3, $Co(NO_3)_2$,dien, H_2O	HT 175 °C, 3 d, pH = 7	EA, IR, SC-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	$K_{8-x}Na_xSiW^{VI}_{11}O_{39}$, $(N(C_4H_9)_4)_{0.5}Na_{1.5}[Mo^{V}_2O_4(H_2O)_2(ox)_2]$, $CuCl_2\cdot 2H_2O$, H_3BTC,	HT 180 °C, 3 d, pH = 4.8	EA, IR, SC-XRD, magnetometry, proton conductivity measurements	nr	[74]
	$H_2[\alpha\text{-}SiMo^{V}_2W^{VI}_{10}O_{40}][Cu(PDA)_2\cdot H_2O]_2$	2	$K_{8-x}Na_xSiW^{VI}_{11}O_{39}$, $(N(C_4H_9)_4)_{0.5}Na_{1.5}[Mo^{V}_2O_4(H_2O)_2(ox)_2]$, $CuCl_2\cdot 2H_2O$, PDA	90 °C	EA, IR, UV-vis, EPR, TGA, SC-XRD, magnetometry	nr	[75]
Ge^{IV}	$H_2[\alpha\text{-}GeMo^{V}_2W^{VI}_{10}O_{40}][Cu(DMF)_3H_2O]_2\cdot 5H_2O$	2	$K_{8-x}Na_xSiW^{VI}_{11}O_{39}$, $(N^nBu_4)_{0.5}Na_{1.5}[Mo^{V}_2O_4(H_2O)_2(ox)_2]$, $CuCl_2\cdot 2H_2O$, DMF	72 °C, pH = 7	EA, IR, SC-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
SC-XRD – single-crystal X-ray diffraction
TGA – thermogravimetric analysis
UV-vis – ultraviolet-visible spectroscopy
XPS – X-ray photoelectron spectroscopy

Organic compounds

bpe – 1,2-bis(4-pyridine)-ethane
bpmb – 1,4-bis(pyrazol-1-ylmethyl)benzene
bipy – bipyridine
btp – 1,3-bis(1,2,4-triazol-1-yl)propane
BTC – 1,3,5-benzenetricarboxylate
btz – 1-benzyl-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-imidazolyl)benzene
ox – oxalate

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

Heteroatom X	Formula	Number of blue e$^-$	Educts	Synthetic conditions	Characterization methods	Application	Ref.
Bi-capped bivanadyl POMos							
P^V	$(N^nBu_4)_3[PMo^V_4Mo^{VI}_8O_{40}(V^{IV}O)_2]$	6	$(N^nBu_4)_3[PMo^{VI}_{12}O_{40}]$, MeCN, $[V^VOCl_3(dme)]$, Na/Hg amalgam	19 h	EA, IR, ^{31}P NMR, CV, SC-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	$NH_4[V^VO_3]$, $H_3[PMo^{VI}_{12}O_{40}]$, $Cu(OAc)_2$, 2,4′-bipy, H_2O	HT 160 °C, 13 d	EA, IR, XPS, SC-XRD	nr	77
	$[\{Co(2,2'\text{-bipy})_2(H_2O)\}_2][PMo^V_5Mo^{VI}_7O_{40}(V^{IV}O)_2]$	7	$Na[V^VO_3]$, $Na_2[Mo^{VI}O_4]$, $Co(NO_3)_2$, 2,2′-bipy, H_3PO_4	HT 160 °C, 5 d, pH = 4.5	EA, IR, UV-vis, SC-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	$NH_4[V^VO_3]$, $H_3[PMo^{VI}_{12}O_{40}]$, $Cu(C_2O_2)_2$, 2,3′-bipy, H_2O	HT 160 °C, 13 d	EA, IR, XPS, SC-XRD	nr	77
	$(NEt_3H)_5[PMo^V_6Mo^{VI}_6O_{40}(V^{IV}O)_2]$	8	$Na_2[Mo^{VI}O_4]$, $V^{IV}OSO_4$, H_3PO_4, NEt_3HCl, H_2O	HT 180 °C, 3 d	EA, IR, UV-vis, SC-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	$Na[V^VO_3]$, $Na_2[Mo^{VI}O_4]$, $Co(NO_3)_2$, phen, H_3PO_4, H_2O	HT 160 °C, 5 d, pH = 4.5	EA, IR, TGA, SC-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	$H_4[SiMo^{VI}_{12}O_{40}]$, $Ni(NO_3)_2$, $NH_4[V^VO_3]$, phen, trea, H_2O	HT 160 °C, 5 d	EA, IR, XPS, TGA, SC-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	$H_4[SiMo^{VI}_{12}O_{40}]$, $Co(NO_3)_2$, $NH_4[V^VO_3]$, phen, trea, H_2O	HT 160 °C, 5 d	EA, IR, XPS, TGA, SC-XRD, magnetometry	nr	80
	$[Cu^I(phen)_2]_2\{[Cu^I(phen)]_2[SiMo^V_4Mo^{VI}_8O_{40}(V^{IV}O)_2]\}$	6	$H_4[SiMo^{VI}_{12}O_{40}]$, $Cu(NO_3)_2$, $NH_4[V^VO_3]$, phen, trea, H_2O	HT 160 °C, 6 d	EA, IR, XPS, CV, TGA, SC-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	$H_4[GeMo^{VI}_{12}O_{40}]$, $Co(NO_3)_2$, $NH_4[V^VO_3]$, phen, trea, H_2O	HT 160 °C, 5 d	EA, IR, XPS, TGA, SC-XRD, magnetometry	nr	80
	$\{[Zn(phen)_2]_2[GeMo^V_4Mo^{VI}_8O_{40}(V^{IV}O)_2]\}\{[Zn(phen)_2(H_2O)]_2[GeMo^V_4Mo^{VI}_8O_{40}(V^{IV}O)_2]\}\cdot 3H_2O$	6	$H_4[GeMo^{VI}_{12}O_{40}]$, $Zn(NO_3)_2$, $NH_4[V^VO_3]$, phen, trea, H_2O	HT 160 °C, 6 d	EA, IR, CV, XPS, TGA, SC-XRD, magnetometry	nr	81
As^V	$[M(2,2'\text{-bipy})_2(H_2O)]_2[AsMo^V_5Mo^{VI}_7O_{40}(V^{IV}O)_2]\}$, M = Co, Zn	7	$Li_3[AsMo^{VI}_{12}O_{40}]$, $M(NO_3)_2$ (M = Co, Zn), $NH_4[V^VO_3]$, 2,2′-bipy, trea, H_2O	HT 160 °C, 6 d	EA, IR, XPS, TGA, SC-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	$Li_3[AsMo^{VI}_{12}O_{40}]$, $Cu(NO_3)_2$, $NH_4[V^VO_3]$, 4,4′-bipy, trea, H_2O	HT 165 °C, 6 d	EA, IR, CV, XPS, TGA, SC-XRD, magnetometry	nr	83

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V^{IV}	$(NEt_4)_4[V^{IV}Mo^{V}_{2}Mo^{VI}_{10}V^{V}_{2}O_{44}]$		$Na_2[Mo^{VI}O_4]$, $V^{V}_{2}O_5$, 1,2,4,5-benzenetetracarboxylic acid, NEt_4Cl, H_2SO_4	HT 180 °C, 3,7 d	EA, IR, SC-XRD	nr	[84]
	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	$H_3PMo^{VI}_{12}O_{40}$, $NH_4[V^{V}O_3]$, $Co(OAc_2)_2$, L, H_2O	HT 160 °C, 3 d	EA, IR, XPS, TGA, powder XRD, SC-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	$Na_2[Mo^{VI}O_4]$, $Na[V^{V}O_3]$, H_3PO_4, $CoCl_2$, bix, H_2O, HCl	HT 160 °C, 5 d, pH = 4	EA, IR, UV-vis, TGA, SC-XRD	photocatalyst for degradation of RhB	[86]
	$[HMn^{II}(bix)_4][PMo^{VI}_{8}V^{V}_{4}O_{40}(V^{IV}O)_2]\cdot 2H_2O$	3	$Na_2[Mo^{VI}O_4]$, $Na[V^{V}O_3]$, H_3PO_4, $Mn(OAc)_2$, bix, H_2O, HCl	HT 170 °C, 6 d, pH = 5.1	EA, IR, UV-vis, TGA, SC-XRD	photocatalyst for degradation of RhB	[87]
	$[M(bix)_4][PMo^{VI}_{9}V^{V}_{3}O_40(V^{IV}O)_2]\cdot 2H_2O$, M = Zn^{II}, Cu^{II}	3	$Na_2[Mo^{VI}O_4]$, $Na[V^{V}O_3]$, H_3PO_4, $M(OAc)_2$, bix, H_2O, HCl	HT 170 °C, 6 d, pH = 5.1	EA, IR, UV-vis, TGA, SC-XRD	photocatalyst for degradation of RhB	[87]
	$[Co(2,2'\text{-bipy})_3]_2[PMo^{VI}_{8}V^{V}_{3}V^{IV}O_{40}(V^{IV}O)_2][\{Co(2,2'\text{-bipy})_2(H_2O)\}_2\{PMo^{VI}_{8}V^{V}_{3}V^{IV}O_{40}(V^{IV}O)_2\}]\cdot 8H_2O$	3	$H_6P_2Mo^{VI}_{18}O_{62}$, $NH_4[V^{V}O_3]$, $CoCl_2$, H_2O	HT 180 °C, 4 d,	EA, IR, XPS, SC-XRD	nr	[88]
P^{V}	$(TEA)_2[PMo^{VI}_{8}V^{IV}_{4}V^{V}_{2}O_{42}][M(phen)_2(H_2O)]_2\cdot H_3O\cdot 3H_2O$ (M = Co, Ni, Zn)	4	$NH_4[V^{V}O_3]$, H_3PO_4, $H_3PMo^{VI}_{12}O_{40}$, M^{2+}, NEt_3, Phen, H_2O	HT 160 °C, 3 d, pH = 6	EA, IR, UV-vis, XPS, SC-XRD	nr	[89]
	$[PMo^{VI}_{8}V^{IV}_{5}V^{V}_{1}O_{42}][Co(phen)_2]_2[Hpy]\cdot 3H_3O\cdot H_2O$	5	$NH_4[V^{V}O_3]$, 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, SC-XRD	nr	[89]
	$[\{PMo^{VI}_{5}Mo^{V}_{3}V^{V}_{4}V^{IV}_{2}O_{42}\}\{Co^{II}(H_2O)(2,2'\text{-bipy})_2\}_2][Co^{II}(2,2'\text{-bipy})_3]_2\{PMo^{VI}_{7}Mo^{V}V^{V}_{6}O_{42}\}\cdot 6H_2O$	5	$Na_2[Mo^{VI}O_4]$, NH_4VO_3, H_3PO_4, $Co(OAc)_2$, 2,2'-py, H_2O	HT 160 °C, 5 d,	EA, IR, TGA, SC-XRD	nr	[90]
	$[\{PMo^{VI}_{6}Mo^{V}_{2}V^{V}_{3}V^{IV}_{3}O_{42}\}\{Cu^{II}(2,2'\text{-bipy})\}\{Cu^{II}(2,2'\text{-bipy})_2\}_2]\cdot 3.5H_2O$	5	$Na_2[Mo^{VI}O_4]$, $NH_4[V^{V}O_3]$, H_3PO_4, $Cu(OAc)_2$, 2,2′-bipy, H_2O	HT 160 °C, 5 d	EA, IR, TGA, SC-XRD	nr	[90]
	$[Co_4(phen)_8(H_2O)_2(HPO_3)_2](H_3O)_3[PMo^{VI}_{8}V^{IV}_{4}O_{40}(V^{IV}O)_2]$	6	$Na_2[Mo^{VI}O_4]$, $NH_4[V^{V}O_3]$, H_3PO_4, $CoCl_2$, phen, H_2O	HT 160 °C, 6 d, pH = 4	EA, IR, UV-vis, XPS, EPR, TGA, SC-XRD	nr	[91]
	$[Cu^{I}(phen)_2]_4[PMo^{VI}_{8}V^{IV}_{6}O_{42}\{Cu^{I}(phen)\}_2]\cdot H_5O_2$	6	$Na_2[Mo^{VI}O_4]$, $NH_4[V^{V}O_3]$, H_3PO_4, $CuCl_2$, phen, H_2O	HT 160 °C, 7 d, pH = 4,4	EA, IR, UV-vis, EPR, TGA, SC-XRD	nr	[53]
V^{V}	$[Ni(enMe)_2][(V^{V}Mo^{V}I_8V^{IV}_{4}O_{40})(V^{IV}O)_2]_2\}\cdot 10H_2O$	6	$Na_2[Mo^{VI}O_4]$, $Na[V^{V}O_3]$, HCl, enMe, $NiCl_2$	HT 160 °C, 4 d, pH = 3,7	EA, IR, UV-vis, SC-XRD	photocatalytic degradation of RhB	[92]

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	$Na_{0.5}K_{6.5}[Mo^{VI}_8V^{IV}_4O_{36}(V^{V}O_4)(V^{IV}O)_2]\cdot 12.5H2O$	6	$Na_2[Mo^{VI}O_4]$, KCl, $V^{IV}OCl_2$, H_2O	45 – 50°C (Ar atm.), 5 d, pH = 6,2	EA, IR, SC-XRD	nr	[93]
Bi-capped bivanadyl POTs and PONs							
V^{IV}	[NiL$_4$$V^{IV}W^{V}_2W^{VI}_{10}O_{40}(V^{IV}O)_2$], L = 1,4-bis(imidazol-1-ylmethyl)benzene	4	$Na_2[W^{VI}O_4]$, V_2O_5, $NiCl_2$, L, H_2O	HT 160 °C, 5 d, pH = 6,5	EA, IR, TGA, SC-XRD	photocatalyst for photodegradation of dyes	[94]
Ge^{IV}	$\{Cu(en)_2\}_6\{GeNb^{V}_{12}V^{IV}_2O_{42}\}\cdot 20H_2O$	2	$K_7HNb_6O_{19}$, $Cu(OAc)_2$, $Na[V^{V}O_3]$, GeO_2, NaOH	HT 160 °C, 3 d, pH = 12	EA, IR, TGA, SC-XRD	antitumor activity	[95]
As^{V}	$[Ni(enMe)_2]_4\{[Ni(enMe)_2][Ni(enMe)_2(H_2O)AsW^{V}_4W^{VI}_6V^{IV}_4O_{42}\}\cdot 6H_2O$	8	Na_3AsO_4, $Na_2[W^{VI}O_4]$, V_2O_5, $NiCl_2$, enMe, H_2O	HT 180 °C, 3 d, pH = 6.5–7	EA, IR, XPS, SC-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	$K_7HNb_6O_{19}$, $Na[V^{V}O_3]$, $CuSO_4$, en	HT 110 °C, 4 d, pH = 12,3	EA, IR, SC-XRD	nr	[96]
Bi-capped with $Mo^{V/VI}$ or Sb^{III} ions POMos							
Si^{IV}	$(NMe_4)_5[SiMo^{V}_4Mo^{VI}_{10}O_{44}]$	4	$[Mo^{VI}_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6]$, Na_2SiO_3, HCl, NMe_4OH, H_2O	HT 150 °C, 36 h, pH = 4	EA, IR, SC-XRD, magnetometry	nr	97
	$(NMe_4)_6[Si_2Mo^{V}_{14}Mo^{VI}_{14}O_{84}(H_2O)]\cdot 2H_2O$	7	$[Mo^{VI}_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6]$, Na_2SiO_3, HCl, NMe_4OH, H_2O	HT 150 °C, 36 h, pH = 2	EA, IR, SC-XRD, magnetometry	nr	97
Al^{III}	$(H_2bpp)_{0.5}(H_2bpp)_2[AlMo^{V}_4Mo^{VI}_8O_{40}(Mo^{VI}O_2)_2]\cdot 2H_2O$	4	$AlCl_3$, $Na_2[Mo^{VI}O_4]$, $NiCl_2$, bpp, H_2O	HT 160 °C, 5 d, pH = 4.3	EA, IR, XPS, SC-XRD	catalytic oxidation of cyclohexanol to cyclohexanone	98
As^{V}	$NH_4[Mo^{VI}_6Mo^{V}_6O_{36}(As^{V}O_4)Mo^{V}(Mo^{V}O)]$	8	$(NH_4)_6Mo^{VI}_7O_{24}$, $NaAsO_2$, NH_4OAc, $N_2H_6SO_4$, $Mn(OAc)_2$, H_2O, HCl	HT 150 °C, 6 d, pH = 0.5	EA, IR, TGA, XPS, SC-XRD	H_2O_2-based oxidation of styrene	99
P^{V}	$(C_2N_2H_9)_2[PMo^{V}_5Mo^{VI}_7Sb^{III}_2O_{40}]\cdot 2H_2O$	5	$(NH_4)_6[Mo^{VI}_7O_{24}]$, Sb_2O_3, H_3PO_4, en, H_2O	HT 185 °C, 3 d, pH = 7	EA, IR, TGA, XPS, SC-XRD	nr	[100]
	$[PMo^{V}_5Mo^{VI}_7Sb^{III}_2O_{40}][M^{II}(enMe)_2]\cdot 4H_2O$, M = Cu, Ni	5	$(NH_4)_6[Mo^{VI}_7O_{24}]$, H_3PO_4, Sb_2O_3, M^{2+}, en, H_2O, HCl	HT 160 °C, 3 d,	EA, IR, TGA, XPS, SC-XRD	nr	[101]
	$(N^{n}Bu_4)_3[PMo^{V}_6Mo^{VI}_6Sb^{III}_2O_{40}]$	6	$(N^{n}Bu_4)_3[PMo^{VI}_{12}O_{40}]$, MECN, $SbCl_3$, Na/Hg amalgam	30 h	EA, IR, ^{31}P NMR, CV, SC-XRD	nr	[52]

nr – not reported **Methods** CV – cyclic voltammetry EA – elemental analysis

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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
SC-XRD – single-crystal X-ray diffraction
TGA – thermogravimetric analysis
UV-vis – ultraviolet-visible spectroscopy
XPS – X-ray photoelectron spectroscopy

Organic compounds

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

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

Heteratom X	Formula	Number of blue e^-	Educts	Synthetic conditions	Characterization methods	Application	Ref.
			$\{XMo_8^{V/VI}V_8^{V/IV}\}$				
P^V	$[Mo^{V}Mo^{VI}_7V^{IV}_8O_{40}(PO_4)][M(phen)_2(OH)]_2[M(phen)_2(OEt)]_2 \cdot xH_2O$ (M = Ni^{II}, Co^{II})	9	$NH_4[V^{V}O_3]$, $H_2Mo^{VI}O_4$, $(NH_4)_2HPO_4$, $M(NO_3)_2$, phen, 1,3-diaminopropane, H_2O, EtOH	HT 170 °C, 20 d	EA, IR, TGA SC-XRD, magnetometry	nr	102
	$[Ni(C_2N_2H_8)_3]_2Na[Mo^{V}_2Mo^{VI}_6V^{IV}_8O_{40}(PO_4)] \cdot H_2O$	10	$NH_4[V^{V}O_3]$, $Na_2[Mo^{VI}O_4]$, H_3PO_4, $Ni(OAc)_2$, en, H_2O	HT 160 °C, 6 d, pH = 6	EA, IR, TGA SC-XRD	nr	103
	$[PMo^{V}_2Mo^{VI}_6V^{IV}_8O_{44}\{Co(2,2'\text{-bipy})_2(H_2O)\}_4]$-$[PMo^{V}_4Mo^{VI}V^{IV}_8O_{44}\{Co(2,2'\text{-bipy})_2(H_2O)\}_2] \cdot 4H_2O$	10	$NH_4[V^{V}O_3]$, $Na_2[Mo^{VI}O_4]$, $CoCl_2$, 2,2′-bipy, H_2O	HT 160 °C, 7 d, pH = 4,2	EA, IR, UV-vis, EPR, SC-XRD	nr	53
	$\{[Ni(phen)_2(H_2O)]_2[Ni(phen)_2][Mo^{V}_2Mo^{VI}_6V^{IV}_8O_{40}(PO_4)]\}$-$\{[Ni(phen)_2(H_2O)]_2[Mo^{V}_2Mo^{VI}_6V^{IV}_8O_{40}(PO_4)_2]\} \cdot 5H_2O \cdot 2EtOH$	10	$NH_4[V^{V}O_3]$, $H_3PMo^{VI}_{12}O_{40}$, $Ni(NO_3)_2$, phen, 1,3-diaminopropane, EtOH, H_2O	HT 170 °C, 6 d	EA, IR, EPR, XPS, SC-XRD, magnetometry	nr	104
	$\{Mo^{V}_2Mo^{VI}_6V^{IV}_8O_{40}(PO_4)[Co(phen)_2(H_2O)]_2\}[Co_2(phen)_2(OH)_2(H_2O)_4]_{1/2}$	10	$NH_4[V^{V}O_3]$, $H_3PMo^{VI}_{12}O_{40}$, $[Co(en)_3]Cl_3$, phen, H_2O	HT 170 °C, 6 d	EA, IR, SC-XRD	nr	105
	$[Co(en)_2][Co(2,2'\text{-bipy})_2]_2[PMo^{V}_3Mo^{VI}_5V^{IV}_8O_{44}] \cdot 4.5H_2O$	11	$NH_4[V^{V}O_3]$, $H_3PMo^{VI}_{12}O_{40}$, $[Co(en)_3]Cl_3$, 2,2′-bipy, H_2O	HT 170 °C, 6 d	EA, IR, XPS, TGA, SC-XRD	nr	106
	$\{Mo^{V}_3Mo^{VI}_5V^{IV}_8O_{40}(PO_4)[Co(phen)(en)(H_2O)]_2\}[Co(phen)_3] \cdot 1.5H_2O$	11	$NH_4[V^{V}O_3]$, $H_3PMo^{VI}_{12}O_{40}$, $Co(C_2O_4)_2$, en, phen, H_2O	HT 170 °C, 10 d	EA, IR, SC-XRD	nr	105
	$[Cu(en)_2]\{[Cu(en)_2]_2[Mo^{V}_3Mo^{VI}_5V^{IV}_8O_{40}(PO_4)]\} \cdot 4H_2O$	11	$(NH_4)_6[Mo^{VI}_7O_{24}]$, $NH_4[V^{V}O_3]$, $V^{IV}O(SO_4)$, H_3PO_3, $CuCl_2$, $H_2C_2O_4$, H_2O	HT 180 °C, 3 d, pH = 9	EA, IR, XPS, TGA, SC-XRD, magnetometry	nr	107
	$\{[M(2,2'\text{-bipy})_2H_2O]_4[Mo^{V}_3Mo^{VI}_5V^{IV}_8O_{40}(PO_4)]\}\{M(2,2'\text{-bipy})_2H_2O]_2[Mo^{V}_3Mo^{VI}_5V^{IV}_8O_{40}(PO_4)]\} \cdot xH_2O$ (M = Ni^{II}, Co^{II})	11	MCl_2, $H_2Mo^{VI}O_4$, V_2O_5, $H_2C_2O_4$, H_3PO_4, 2,2′-bipy, H_2O	HT 175 °C, 5 d,	EA, IR, EPR, XPS, SC-XRD, magnetometry	nr	108
	$\{[Mo^{V}_3Mo^{VI}_5V^{IV}_8O_{40}(PO_4)][Ni(en)_2]\}[Ni(en)_2]_2 \cdot 4H_2O$	11	$NH_4[V^{V}O_3]$, $H_3PMo^{VI}_{12}O_{40}$, $Ni(NO_3)_2$, en, H_2O	HT 170 °C, 10 d	EA, IR, SC-XRD	nr	109
	$[Co(en)_2]\{[Co(en)_2]_2[HMo^{V}_4Mo^{VI}_4V^{IV}_8O_{40}(PO_4)]\} \cdot 5H_2O$	12	$(NH_4)_6[Mo^{VI}_7O_{24}]$, $NH_4[V^{V}O_3]$, $VO(SO_4)$, H_3PO_3, $CoCl_2$, $H_2C_2O_4$, H_2O	HT 180 °C, 3 d, pH = 9	EA, IR, XPS, SC-XRD, magnetometry	nr	107
	$\{[Co(phen)_2]_2C_2O_4\}\{H_2PMo^{V}_5Mo^{VI}_3V^{IV}_8O_{44}[Co(phen)_2H_2O]_2\} \cdot 7H_2O$	13	$NH_4[V^{V}O_3]$, $Na_2[Mo^{VI}O_4]$, $CoCl_2$, $H_2C_2O_4$, H_3PO_4, phen, H_2O	HT 160 °C, 3 d, pH = 9	EA, IR, EPR, XPS, SC-XRD, magnetometry	nr	110

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	$[Ni(en)_2]\{[Ni(en)_2]_2[Mo^{V}_3Mo^{VI}_5V^{IV}_8O_{40}(V^{V}O_4)]\}\cdot 2H_2O$	11	$(NH_4)_6[Mo^{VI}_7O_{24}]$, $NH_4[V^{V}O_3]$, $V^{IV}O(SO_4)$, H_3PO_3, $Ni_2C_2O_4$, $H_2C_2O_4$, H_2O	HT 180 °C, 3 d, pH = 9	EA, IR, XPS, TGA, SC-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	$Na[V^{V}O_3]$, $Na_2[Mo^{VI}O_4]$, $NiCl_2$, enMe, HCl, H_2O	HT 160 °C, 4 d, pH = 3.6	EA, IR, UV-vis, SC-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	$V^{V}_2O_5$, $Mo^{VI}O_3$, $NiCl_2$,enMe, H2O	HT 160 °C, 4 d	EA, IR, EPR, SC-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	$NH_4[V^{V}O_3]$, $H_3AsMo_{12}O_{40}$, $Co(en)_3Cl_3$, H_2O	HT 180 °C, 6 d	EA, IR, EPR, SC-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, $(NH_4)_6[Mo^{VI}_7O_{24}]$, V_2O_5, $NiCl_2$, enMe, $H_2C_2O_4$, H_2O	HT 180 °C, 3 d, pH = 6.5–7	EA, IR, XPS, SC-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
SC-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
bipy – bipyridine
bipy – bipyridine
en – ethylenediamine
enMe – 1,2-diaminopropane
Et – ethyl
phen – 1,10-phenanthroline
RhB – rhodamine B

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

Heteroatom X	Formula	Number of blue e$^-$	Educts	Synthetic conditions	Characterization methods	Application	Ref.
			{$X_2Mo_{18}O_{62}$}				
SO_3^{2-}	$(NEt_4)_6[Mo^{V}_2Mo^{VI}_{16}O_{54}(SO_3)_2]\cdot 4H_2O$	2	NEt_4OH, $Na_2[Mo^{VI}O_4]$, $Na_2S_2O_4$, HCl, H_2O	pH = 4, 1 h	EA, IR, UV-vis, SC-XRD, BVS, redox titration	nr	[113]
	$(N^nBu_4)_5[S_2Mo^{V}Mo^{VI}_{17}O_{62}]$	1	$(N^nBu_4)_4[S_2Mo^{VI}_{18}O_{62}]$, $^n Bu_4NClO_4$	electrolysis at 400 mV vs. Ag/AgCl	EA, IR, EPR	nr	114
	$(C_{16}H_{18}N_3S)_5[S_2Mo^{V}Mo^{VI}_{17}O_{62}]\cdot MeCN$	1	$(N^nBu_4)_4[S_2Mo^{VI}_{18}O_{62}]$, MeCN, MB	RT	EA, IR, XPS, SC-XRD, magnetometry	reduction of NO_2^-, ClO_3^-, BrO_3^-, H_2O_2	115
SO_4^{2-}	$[Fe^{III}(C_5Me_5)_2]_5[HS_2Mo^{V}_2Mo^{VI}_{16}O_{62}]\cdot 3DMF\cdot 2\ Et_2O$	2	$[Fe^{II}(C_5Me_5)_2]$, $(NHex_4)_4[S_2Mo_{18}O_{62}]$, MeCN	RT	EA, IR, ^{1}H NMR, EPR, CV, SC-XRD, magnetometry		116
	$(N^nBu_4)_6[S_2Mo^{V}_2Mo^{VI}_{16}O_{62}]$	2	$(N^nBu_4)_4[S_2Mo^{VI}_{18}O_{62}]$, $N^nBu_4ClO_4$	electrolysis at 0 mV vs. Ag–AgCl	EA, IR, EPR	nr	114
	$(N^nBu_4)_5[H_3S_2Mo^{V}_4Mo^{VI}_{12}O_{62}]\cdot 4\ MeCN$	4	PPh_3, $(N^nBu_4)_4[S_2Mo^{VI}_{18}O_{62}]$, MeCN·	reflux, 72 h	EA, IR, UV-vis SC-XRD	nr	117
AsO_4^{3-}	$[Cu(2,2'\text{-bipy})_2][\{Cu(2,2'\text{-bipy})\}_3\{As^{V}_2Mo^{V}_2Mo^{VI}_{16}O_{62}\}]\cdot 4H_2O$	2	$(NH_4)_6[Mo^{VI}_7O_{24}]$, $NaAsO_2$, 2,2′-bipy, $CuCl_2$, HCl	HT 160 °C, 3 d, pH = 4	EA, IR, UV-vis, XPS, PXRD, SC-XRD	electrocatalyst for the reduction of NO_2^-	[118]
	$[H_2(4,4'\text{-bipy})]_{2.5}[As^{III}(As^{V}_2Mo^{V}_2Mo^{VI}_{16}O_{62})]\cdot 5H_2O$	2	$(NH_4)_6[Mo^{VI}_7O_{24}]$, $NaAsO_2$, 4,4′-bipy, $CuCl_2$, HCl	HT 160 °C, 3 d, pH = 3	EA, IR, UV-vis, XPS, PXRD, SC-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	$(NH_4)_6[Mo^{VI}_7O_{24}]$, $NaAsO_2$, imi, $CuCl_2$, HCl	HT 160 °C, 3 d, pH = 2.5	EA, IR, UV-vis, XPS, PXRD, SC-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	$(NH_4)_6[Mo^{VI}_7O_{24}]$, $NaAsO_2$, imi, $CuCl_2$, HCl	HT 160 °C, 3 d, pH = 2	EA, IR, UV-vis, XPS, PXRD, SC-XRD	electrocatalyst for the reduction of NO_2^-	[118]
			{$X_2W_{18}O_{62}$}				
SO_3^{2-}	$(NPr_4)_5\{\alpha\text{-}[W^{V}W^{VI}_{17}O_{54}(SO_3)_2]\}\cdot 2\ MeCN$	1	$K_7Na[W^{VI}_{18}O_{56}(S^{IV}O_3)_2(H_2O)_2]\cdot 20H_2O$, $Na_2S_2O_4$, N^nPr_4Br, HCl	RT, pH = 1	EA, IR, EPR, SC-XRD, electrochemistry, photochemistry	nr	[119]
ClO_4^-	$(N^nBu_4)_3[Cl_2W^{V}W^{VI}_{17}O_{62}]$	1	$Na_2[W^{VI}O_4]$, DMF, HCl, N^nBu_4Br	UV irridation,	EA, IR, EPR, CV, SC-XRD	nr	[120]

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AsO_4^{3-}	$[Cu_4(btb)_6(H_2O)_2][As_2W^{V}_2W^{VI}_{16}O_{62}]\cdot 10H_2O$	2	α-$K_6As_2W^{VI}_{18}O_{62}$, $Cu(NO_3)_2$, btb, NEt_3	HT 170 °C, 4 d, pH = 3.8	EA, IR, SC-XRD, electrochemistry, photochemistry	electrocatalyst for the reduction of NO_2^-; photocatalytic degradation of MB	121
	$\{X_2M_{18}O_{62}\}$						
	$(N^nBu_4)_7[P_2Mo^{V}Mo^{VI}_nW^{VI}_{17-n}O_{62}]$, n = 0, 1, 2	1	$(N^nBu_4)_7[P_2Mo^{VI}_nW^{VI}_{18-n}O_{62}]$ (n = 1 – 3), DMF	irridation by a Hg lamp	EA, IR, redox titration, ^{31}P NMR, magnetometry	nr	122
PO_4^{3-}	$K_8[V^{IV}OP_2Mo_2W_{15}O_{61}]\cdot 16H_2O$	1	$K_{10}[P_2Mo_2W_{15}O_{61}]\cdot 19H_2O$, HOAc, LiOH, LiCl, $VOSO_4$, KCl		EA, IR, UV-vis, ^{31}P NMR, CV	nr	123
	$K_9[H_4PV^{IV}W_{17}O_{62}]\cdot 18H_2O$	1	$VOSO_4$, $K_{11}[H_4PW_{17}O_{61}]\cdot 18H_2O$, HCl, KCl		EA, IR, UV-vis, ^{31}P NMR, CV	oxidation of L-cysteine	124
AsO_3^{3-}	$K_8[V^{IV}OAs_2W_{17}O_{61}]\cdot 16H_2O$	1	$[As_2W_{17}O_{61}]^{6-}$, $V^{IV}OSO_4$		EA, IR, UV-vis, ^{31}P NMR, CV	nr	125
SO_3^{2-}	$(NH_4)_7[Mo^{VI}_{11}V^{V}_5V^{IV}_2O_{52}(SO_3)]\cdot 12H_2O$		$(NH_4)_6[Mo^{VI}_7O_{24}]\cdot 4H_2O$, HCl, $NH_4[V^{V}O_3]$, $(NH_4)_2SO_3$	pH = 1,5	EA, IR, CSI-MS, EPR, SC-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
SC-XRD – single-crystal X-ray diffraction
UV-vis – ultraviolet-visible spectroscopy
XPS – X-ray photoelectron spectroscopy
Organic compounds
Bu – butyl
bipy – bipyridine
btb – 1,4-bis(1,2,4-triazol-1-yl)butane
DMF – N,N-dimethylforamide
imi – imidazol
MB – methylene blue
Me – methyl
Pr – isopropyl
PPh_3 – tiphenylphosphine
pyr – pyridine
TEAH – triethanolamine

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

M^{n+}	Formula	Number of blue e^-	Educts	Synthetic conditions	Characterization methods	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	$Mo^{VI}O_3$, Mo^0, dmpip, KH_2PO_4,H_3PO_4, H_2O	HT 150 °C, 5 d	EA, IR, UV-vis, CV, SC-XRD	nr	[127]
	$[Cu_4(2,2'\text{-bipy})_4(H_2O)_4K\subset P_6Mo_{18}O_{71}(OH)_2]\cdot 7H_2O$	3	$Mo^{VI}O_3$, Mo^0, CuO, 2,2′-bipy, KH_2PO_4,H_3PO_4, H_2O	HT 150 °C, 5 d	EA, IR, SC-XRD, DFT calculation	nr	[128]
Ca^{2+}	$\{[Cu(2,2'\text{-bipy})(H_2O)]_4[Ca\subset P_6Mo^{V}_2Mo^{VI}_{16}O_{73}]\}\cdot 4H_2O$	2	$Na_2[Mo^{VI}O_4]$, $CuCl_2$, $CaCl_2$, H_3PO_4, NaOH, 2,2′-bipy, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV-vis, XPS, SC-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	$(NH_4)_6[Mo^{VI}_7O_{24}]$, $Cu(OAc)_2$, H_3PO_4, $CaCl_2$, bih, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV-vis, XPS, SC-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	$(NH_4)_6[Mo^{VI}_7O_{24}]$, $Fe(OAc)_2$, H_3PO_4, $CaCl_2$, bib, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV-vis, XPS, SC-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	$Na_2[Mo^{VI}O_4]$, $CuCl_2$, $CaCl_2$, H_3PO_4, NaOH, bim, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV-vis, XPS, SC-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	$(NH_4)_6[Mo^{VI}_7O_{24}]$, $Cu(OAc)_2$, H_3PO_4, $CaCl_2$, en, H_2O	HT 160 °C, 4 d, pH = 3	EA, IR, TGA, UV-vis, XPS, SC-XRD	photocatalytic degradation of methyl orange, methylene blue, and RhB	[130]
Sr^{2+}	$\{H_2(4,4'\text{-bipy})\}_5\{[Ni(4,4'\text{-bipy})(H_2O)_3]_2[Ni(H_2O)_2][Sr\subset P_6Mo^{V}_2Mo^{VI}_{16}O_{73}]_2\}\cdot 12H_2O$	2	$Na_2[Mo^{VI}O_4]$, $NiCl_2$, $SrCl_2$, H_3PO_4, NaOH, 4,4′-bipy, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV-vis, XPS, SC-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	$(NH_4)_6[Mo^{VI}_7O_{24}]$, $MnAc_2$, H_3PO_4, $SrCl_2$, bth, H_2O	HT 160 °C, 4 d, pH = 3	EA, IR, TGA, UV-vis, XPS, PXRD, SC-XRD	photocatalytic degradation of MB, RhB, and AP; electrocatalytic reduction of NO_2^- and oxidation of ascorbic acid	[131]

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$(H_2L)[\{M^{II}(H_2O)_n\}_2\{Sr \subset P_6Mo^{V}_2Mo^{VI}_{16}O_{73}\}]\cdot xH_2O$ (L = bth, bih, bip; M = Fe, Co, Ni, Cu, Zn)	2	$(NH_4)_6[Mo^{VI}_7O_{24}]$, M^{2+}, H_3PO_4, $SrCl_2$, L, H_2O	HT 160 °C, 4 d, pH = 3	EA, IR, TGA, UV-vis, XPS, PXRD, SC-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	$(NH_4)_6[Mo^{VI}_7O_{24}]$, M^{2+}, H_3PO_4, $SrCl_2$, bib, H_2O	HT 160 °C, 4 d, pH = 3	EA, IR, TGA, UV-vis, XPS, PXRD, SC-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	$Na_2[Mo^{VI}O_4]$, 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, SC-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	$Na_2[Mo^{VI}O_4]$, $FeSO_4$, $SrCl_2$, H_3PO_4, pytp, pytty, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV-vis, XPS, SC-XRD	photocatalytic degradation of MB; electrocatalytic reduction of H_2O_2 and oxidation of dopamine	[134]
$(C_{10}H_{10}N_2)_{12}(PMo^{VI}_{12}O_{40})2(Sr \subset P_6Mo^{V}_3Mo^{VI}_{15}O_{73})2\cdot 9H_2O$	3	$Na_2[Mo^{VI}O_4]$, $SrCl_2$, H_3PO_4, 4,4′-bipy, H_2O	HT 160 °C, 4 d, pH = 3	EA, IR, TGA, UV-vis, XPS, PXRD, SC-XRD	electrocatalytic reduction of NO_2^-	[135]
$\{H_3O\}_2\{Fe^{III}(2,2'\text{-bipy})_3\}_6\{Sr \subset P_6Mo^{V}_4Mo^{VI}_{14}O_{73}\}_2\cdot 9H_2O$	4	$Na_2[Mo^{VI}O_4]$, $FeSO_4$, $SrCl_2$, H_3PO_4, NaOH, 2,2′-bipy, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV-vis, XPS, SC-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	$Na_2[Mo^{VI}O_4]$, $CdCO_3$, $SrCl_2$, H_3PO_4, NaOH, phen, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV-vis, XPS, SC-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	$Na_2[Mo^{VI}O_4]$, $CuCl_2$, $SrCl_2$, H_3PO_4, phen, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV-vis, XPS, SC-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	$Na_2[Mo^{VI}O_4]$, $Mn(OAc)_2$, $SrCl_2$, H_3PO_4, pytty, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV-vis, XPS, SC-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	$(NH_4)_6[Mo^{VI}_7O_{24}]$, H_3PO_4, $SrCl_2$, imi, H_2O	HT 160 °C, 4 d, pH = 3.5	EA, IR, TGA, UV-vis, XPS, PXRD, SC-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	$(NH_4)_6[Mo^{VI}_7O_{24}]$, $M(OAc)_2$, H_3PO_4, $SrCl_2$, bth, H_2O	HT 160 °C, 5 d, pH = 3.5	EA, IR, TGA, UV-vis, XPS, BET, PXRD, SC-XRD	photocatalytic degradation of MB; electrocatalytic reduction of NO_2^-	[138]

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	$(H_2pytty)_2[\{Cd(H_2O)_4\}\{Cd(H_2O)_3(H_3pytty)\}\{Sr \subset P_6Mo^{V}_5Mo^{VI}_{30}O_{73}\}]\cdot 9H_2O$	5	$Na_2[Mo^{VI}O_4]$, $Cd(OAc)_2$, $SrCl_2$, H_3PO_4, pytty, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV-vis, XPS, SC-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	$Na_2[Mo^{VI}O_4]$, $Mn(OAc)_2$, $SrCl_2$, H_3PO_4, pytty, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV-vis, XPS, SC-XRD	photocatalytic degradation of MB; electrocatalytic reduction of H_2O_2 and oxidation of dopamine	134
Ba^{2+}	$\{[Cu(2,2'\text{-bipy})(H_2O)]_4[Ba \subset P_6Mo^{V}_2Mo^{VI}_{16}O_{73}]\}\cdot 8H_2O$	2	$Na_2[Mo^{VI}O_4]$, $CuCl_2$, $BaCl_2$, H_3PO_4, NaOH, phen, H_2O	HT 160 °C, 4 d, pH = 3,5	EA, IR, TGA, UV-vis, XPS, SC-XRD	electrocatalytic reduction of NO_2^-	129
	$\{M\subset(SO_3)_2(PhPO_3)_4Mo^{V/VI}_{18}O_{49}\}$						
Na^+	$(N^nBu_4)_5[Na(SO_3)_2(PhPO_3)_4Mo^{V}_4Mo^{VI}_{14}O_{49}]\cdot n$MeCN	4	$Na_2[Mo^{VI}O_4]$, HCl, $Na_2S_2O_4$, $PhPO_3H_2$, MeCN, N^nBu_4Br	RT	EA, IR, TGA, UV-vis, ^{31}P-NMR, SC-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	$Mo^{VI}O_3$, Mo^0, H_3BO_3, $C_3N_2H_4$, H_3PO_4, HCl, H_2O	HT 165 °C, 5 d,	EA, IR, XPS, SC-XRD	nr	141
	$(C_3N_2H_5)_5[Mo^{V}_5Mo^{VI}_7O_{30}(BPO_4)_2(PhPO_3)_6]\cdot H_2O$	5	$Mo^{VI}O_3$, Mo^0, H_3BO_3, $PhP(O)(OH)_2$, $C_3N_2H_4$, HCl, H_2O	HT 180 °C, 5 d, pH = 1	EA, IR, UV-vis, EPR, SC-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
SC-XRD – single-crystal X-ray diffraction
TGA – thermogravimetric analysis
UV-vis – ultraviolet-visible spectroscopy
XPS – X-ray photoelectron spectroscopy
Organic compounds
bipy – bipyridine
bib – 1,4-bis(1-imidazolyl)butane
bim – 2,2′-biimidazole
bip – 1,5-bis(1-imidazolyl)pentane
bih – 1,6-bis(1-imidazolyl)hexane
bth – 1,6-bis(1-triazolyl)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-(1*H*-1,2,4-triazol-3-yl)-1,2,4-triazole
RhB – rhodamine B

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

Heteroatom	Formula	Number of blue e^-	Educts	Synthetic conditions	Characterization methods	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, MeCN, EtOH, $\{C_2H_4OH\}_3N$	HT 145 °C, 67 h	EA, IR, TGA, SC-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, MeCN, EtOH, $\{C_2H_4OH\}_3N$	HT 145 °C, 24 h	EA, IR, TGA, SC-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, $(HOCH_2CH_2)_2NCH_2CH_2NH_2$	HT 145 °C, 24 h	EA, IR, UV-vis, TGA, CV, SC-XRD	nr	[144]
Mg	$[MgV^{IV}_6O_6\{(OCH_2CH_2)_2N(CH_2CH_2OH)\}_6]2Br{\cdot}H_2O$	6	$(N^nBu_4)_6[V^{V}_{10}O_{28}]$, $MgBr_2$, MeCN, EtOH, $\{C_2H_4OH\}_3N$	HT 155 °C, 6 h	EA, IR, TGA, SC-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	$(NH_4)_6[V^{V}_{10}O_{28}]{\cdot}6H_2O$, MCl_2, MeCN, EtOH, $N\{C_2H_4OH\}_3$	HT 145 °C, 26 h	EA, IR, TGA, SC-XRD, magnetometry	nr	[143]
Mn^{II}	$[Mn^{II}V^{IV}_6O_6\{(OCH_2CH_2)_2N(CH_2CH_2OH)\}_6]Cl_2$	6	$(HOCH_2CH_2)_3N$, $(N^nBu_4)_3[H_3V^{V}_{10}O_{28}]$, $MnCl_2$ 1,3,5-$(HO_2C)_3C_6H_3$, MeCN, MeOH	HT 145 °C, 24 h	EA, IR, SC-XRD,	nr	[145]
V^{V}	$(NH_2Et_2)_4\{[V^{IV}_6O_6(OMe)_9(V^{V}O_3)(H_2O)]_4(L)_6\}$(Solvent), L = BDC, BDC-$NH_2$; Solvent = DEF, MeOH	6	$V^{III}Cl_3$, H_2L, DEF, MeOH, H_2O	HT 130 °C, 2 d	EA, IR, TGA, XPRD, SC-XRD, magnetometry	nr	[146]
S^{VI}	$(NEt_2H_2)_8\{[V^{IV}_6O_6(OMe)_9(SO_4)]_4(L)_6\}$(Solvent), L = BDC, BDC-$NH_2$, BDC-Br; Solvent = DEF	6	$V^{IV}OSO_4$, H_2L, DEF, MeOH, H_2O	HT 130 °C, 2 d	EA, IR, TGA, XPS, SC-XRD, magnetometry	nr	[147]
C^{IV}	$(NH_4)_5[(V^{IV}O)_6(CO_3)_4(OH)_9]{\cdot}10H_2O$	6	$V^{IV}OCl_2$, NH_4HCO_3, CO_2	pH = 7.6 – 7.8	EA, IR, SC-XRD	nr	[148]
–	$[V^{IV}_6O_6\{(OCH_2CH_2)_2N(CH_2CH_2OH)\}_6]{\cdot}0.5MeCN$	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, SC-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	$Na_2[Mo^{VI}O_4]$, Mo^0, H_3PO_4, PPh_4Br, H_2O	HT 130 °C, 1 d	EA, IR, SC-XRD	nr	[150]
	$(NEt_4)_6[Na_{14}\{Mo^{V}_6P_4O_{24}(OH)_7\}_4P(OH)_3]{\cdot}xH_2O$	6	$Na_2[Mo^{VI}O_4]$, Mo^0, H_3PO_4, NEt_4OH, H_2O	HT 200 °C, 3 d	EA, IR, SC-XRD	nr	[151]

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	$Na_2Cd_3(Mo_2O_4OH)_6(PO_4)_2(PO_3OH)_6[NMe_4]_4\cdot 10H_2O$ + $Cd_9(Mo_2O_4OH)_{12}(PO_4)_6(PO_3OH)_{10}[NMe_4]_8\cdot 15H_2O$	6	$Na_2[Mo^{VI}O_4]$, Mo^0, CdO, H_3PO_4, NMe_4OH, and H_2O	HT 220 °C, 1.5 d	EA, IR, SC-XRD	nr	[152]
	$Na_8(Mo^V_2O_4OH)_3(PO_4)_3(PO_3OH)\cdot 12.25H_2O$	6	$Na_2[Mo^{VI}O_4]$, Mo^0, H_3PO_4, NaOH, and H_2O	HT 220 °C, 1.5 d	EA, IR, TGA, SC-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, SC-XRD	nr	[154]
	(4,4′-H_2bipy)[Ni(4,4′-bipy)$(H_2O)_2Ni_{0.5}$-$Mo^V_6(OH)_3O_{12}(HPO_4)_4]\cdot 2H_2O$	6	$NiSO_4$, $Mo^{VI}O_3$, Mo^0, $(NH_4)H_2PO_4$, 4,4′-bipy, H_2O	HT 160 °C, 3 d	EA, IR, TGA, SC-XRD, magnetometry	nr	[155]
	$(NMe_4)_2(cat)_2[M_n\{Mo^V_6O_{15}(HPO_4)(H_2PO_4)_3\}_2]\cdot xH_2O$ (M = Zn^{II}, n = 3, Cat = H_3O^+; M = Fe^{III}, n = 2, cat = NH_4)	12	$Na_2[Mo^{VI}O_4]$, Mo^0, ZnO or $FeCl_3$, NMe_4OH, H_3PO_4, and H_2O	HT 200 °C, 6 d	EA, IR, SC-XRD	nr	[156, 157]
	$(NEt_4)_2Na_3(H_3O)_4\{(Na[(Mo^V_6O_{15}(O_3PC_6H_5)(HO_3PC_6H_5)_3]_2\}\cdot\sim 14H_2O$	12	$Na_2[Mo^{VI}O_4]$, Mo^0, $C_6H_5PO_3H_2$, NEt_4OH, H_3PO_4, and H_2O	HT 200 °C, 3 d	EA, IR, SC-XRD	nr	[158]
	$(NH_4)_5Na_4\{Na[Mo^V_6O_{12}(OH)_3(O_3PC_6H_5)_4]_2\}\cdot 6H_2O$	12	$Na_2[Mo^{VI}O_4]$, Mo^0, $C_6H_5PO_3H_2$, KCl, NH_4Cl, and H_2O	HT 180 °C, 3 d	EA, IR, SC-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	$Na_2[Mo^{VI}O_4]$, 1,3,5-$(HO_2C)_3C_6H_3$, H_3PO_4, $Na_2S_2O_4$	2 h, pH = 3.5	EA, IR, TGA, SC-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	$MnSO_4$, $Na_2[Mo^{VI}O_4]$, H_3PO_4, Mo^0, $H_2N(CH_2)_2NH_2$, H_2O	HT 250 °C, 51 h	EA, IR, TGA, DSC, SC-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	$(NH_4)_6[Mo^{VI}_7O_{24}]\cdot H_2O$, $Co(OAc)_2\cdot 2H_2O$, $KOAc\cdot H_2O$, 2,2′-bipy, H_3PO_4, H_2O	HT 160 °C, 4 d	EA, IR, TGA, UV-vis, SC-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	$Na_2[Mo^{VI}O_4]$, $NiCl_2$, H_3PO_4, bpp, H_2O	HT 180 °C, 5 d, pH = 1.5	EA, IR, TGA, UV-vis, PXRD, SC-XRD	reduction of $[Fe(CN)_6]^{3-}$	[163]
	$(H_2bpp)_5\{Cd[Mo^V_6O_{15}(HPO_4)_3(H_2PO_4)]_2\}\{Cd[Mo^V_6O_{15}(HPO_4)_4]2\}\cdot 10H_2O$	12	$Na_2[Mo^{VI}O_4]$, $CdCl_2$, H_3PO_4, bpp, H_2O	HT 180 °C, 5 d, pH = 1.5	EA, IR, TGA, UV-vis, PXRD, SC-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	$Na_2[Mo^{VI}O_4]$, $CdCl_2$, H_3PO_4, bpp, H_2O	HT 180 °C, 5 d, pH = 0.8	EA, IR, TGA, UV-vis, PXRD, SC-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, SC-XRD	nr	[154]

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C^{IV}	$(NH_4)_5[(Mo^{V}_2O_4)_3(CO_3)_4(OH)_3]\cdot 0.5MeOH$	6	NH_4HCO_3, $Mo^{V}Cl_5$, H_2O	pH = 8	EA, IR, SC-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	$Na_2[Mo^{VI}O_4]$, Mo^0, H_3PO_4, $CoCl_2$, H_2O, HCl	HT 180 °C, 3 d, pH = 2	EA, IR, SC-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	$Na_2[Mo^{VI}O_4]$, Mo^0, H_3PO_4, $CoCl_2$, H_2O, HCl	HT 180 °C, 3 d, pH = 3.9	EA, IR, SC-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	$Na_2[Mo^{VI}O_4]$, Mo^0, H_3PO_4, $NiCl_2$, H_2O, HCl	HT 130 °C, 9 d, pH = 3.3	EA, IR, SC-XRD, magnetometry	nr	[166]
	$[H_2en]_3Na_4[Ni(H_2O)_3][H_{30}(Mo^{V}_{16}O_{32})Ni_{14}(PO_4)_{26}O_2(OH)_4(H_2O)_8]\cdot 8H_2O$	16	$Na_2[Mo^{VI}O_4]$, H_3PO_4, $Ni(OAc)_2$, H_2O, ethylenediaminetetraacetic acid	HT 180 °C, 7 d, pH = 3-4	EA, IR, SC-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	$Na_2[Mo^{VI}O_4]$, H_3PO_4, 4,4′-bipy, pyridine, H_2O, NaOH	HT 165 °C, 5 d, pH = 2.5	EA, IR, TGA, SC-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
SC-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
bipy – bipyridine
DEF - N,N-diethylformamide
Et – ethyl
H_2BDC – 1,4-benzenedicarboxylate
$H_2BDC–NH_2$ – 2-amino-1,4-benzenedicarboxylate
Me – methyl

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