Supporting Information

Vanadoborates: Cluster-based architectures, preparation and properties

Xing Liu, Jian Zhou*, Tatiana R. Amarante, Filipe A. Almeida Paz, Lianshe Fu

Table S1 Conditions used for the syntheses of crystalline vanadoborates.

Classification	Compounds	Reactants	Synthetic methods	D	Ref.
$[V_6B_{20}]$	$[H_3O]_7\cdot[H_2en]_4[(VO)_6(B_{10}O_{22})_2]$ (**1**)	H_3BO_3+$H_2C_2O_4$+$VOSO_4$+H_2SO_4+V_2O_5+$Na_2S_2O_4$+H_2O+en	Hydrothermal reaction	0	16a
	$[Rb_4(VO)_6\{B_{10}O_{16}(OH)_6\}_2]\cdot 0.5H_2O$ (**2**)	$RbVO_3$+$(NH_4)_2B_4O_7\cdot 4H_2O$+$H_2O$+en	Hydrothermal reaction	0	24
	$\{V_6B_{20}O_{42}(OH)_8(H_2O)[K_8(H_2O)_6]\}$ (**3**)	NH_4VO_3+H_3BO_3+K_2SO_3+Ni+dien+H_2O	Hydrothermal reaction	0	18i
	$[H_3dien]_2\{V_6B_{20}O_{42}(OH)_8(H_2O)[K(H_2O)]_2\}\cdot 6H_2O$ (**4**)	NH_4VO_3+H_3BO_3+K_2SO_3+Co+dien+H_2O	Hydrothermal reaction	0	18i
	$[Zn_2(H_2dien)_4(VO)_6\{B_{10}O_{19}(OH)_3\}_2]\cdot(H_2O)_{0.29}$ (**5**)	NH_4VO_3+$NH_4B_5O_8\cdot 4H_2O$+H_3BO_3+$Zn(NO_3)_2\cdot 6H_2O$+dien+H_2O	Hydrothermal reaction	2	25
$[V_6B_{22}]$	$[H_4teta]_2[V_6B_{22}O_{44}(OH)_{10}]\cdot 4.5H_2O$ (**6**)	NH_4VO_3+H_3BO_3+$CuCl_2\cdot 2H_2O$+teta+H_2O	Hydrothermal reaction	0	18a
	$[H_4tepa]_2[B_{22}V_6O_{44}(OH)_{10}]\cdot 4H_2O$ (**7**)	NH_4VO_3+H_3BO_3+$CuCl_2\cdot 2H_2O$+tepa+H_2O	Hydrothermal reaction	0	18a
	$[H_3O]_2\cdot[H_3dien]_2[V_6B_{22}O_{44}(OH)_{10}(H_2O)_{0.5}]\cdot 12H_2O$ (**8**)	$NaVO_3$+B_2O_3+$Ni(OAc)_2$+dien+H_2O	Hydrothermal reaction	0	16b
	$[H_2en]_4[Hen]_2[V_6B_{22}O_{53}H_8]\cdot 5H_2O$ (**9**)	V_2O_5+en+H_3BO_3	Flux synthesis	1	22a
$[V_{10}B_{20}]$	$[H_3dien][(eg)_4V_{10}B_{20}O_{64}]\cdot x$(dien) (**10**)	NH_4VO_3+$NH_4B_5O_8\cdot 4H_2O$+dien+eg	Solvothermal reaction	3	16d
$[V_{10}B_{24}]$	$[1,3\text{-}dapH_2]_5[(1,3\text{-}dapH_2)V_{10}B_{24}O_{66}H_8]\cdot 13.23H_2O$ (**11**)	V_2O_5+$(H_3C)B(OH)_2$+1,3-diap	Flux synthesis	0	16c
	$[(eg)_2V_{10}B_{24}O_{62}]\cdot x$(tepa) (**12**)	NH_4VO_3+H_3BO_3+$NH_4B_5O_8\cdot 4H_2O$+tepa+eg	Solvothermal reaction	1	16d
$[V_{10}B_{28}]$	$[K_6(H_2O)_{10}Zn_4V_{10}B_{32}O_{74}(OH)_{10}]\cdot 5H_2O$ (**13**)	NH_4VO_3+H_3BO_3+$Zn(Ac)_2\cdot 2H_2O$+ea+H_2O+K_2SO_3	Hydrothermal reaction	0	18b
	$[H_3O]_{14}[Mn_4(C_2O_4)_3(V_{10}B_{28}O_{74}H_8)]\cdot 32H_2O$ (**14**)	$Mn(OAc)_2$+V_2O_5+en+H_3BO_3+$C_2O_4H_2$+H_2O	Hydrothermal reaction	0	17a
	$[H_2dap]_4[Zn_4V_{10}B_{34}O_{84}H_{10}]$ $(dap)_2\cdot 9H_2O$ (**15**)	NH_4VO_3+H_3BO_3+ZnO+dap+H_2O	Hydrothermal reaction	0	18g
	$[K_6(H_3O)_8][Mn_4(C_2O_4)(V_{10}B_{28}O_{74}H_8)(B_4O_9H_2)]\cdot 24H_2O$ (**16**)	$KMnO_4$+V_2O_5+en+H_3BO_3	Solvothermal reaction	1	17a
	$Na_2(H_2en)_2\{(VO)_{10}[B_{14}O_{30}(OH)_2]_2\}\{Mn_4(C_2O_4)\text{-}[B_2O_4(OH)_2]_2\}Mn(H_2O)_2\cdot(H_3O)_{12}(H_2O)_{19}$ (**17**)	H_3BO_3+$VOSO_4$+en+$H_2C_2O_4\cdot 2H_2O$+Mn+H_2O	Hydrothermal reaction	1	17b
	$[Zn(en)_2]_2[Zn(OH_2)(en)]_4[Zn_4(B_2O_4H_2)\text{-}(BO_2H)_2(V_{10}B_{28}O_{74}H_8)]\cdot 10H_2O$ (**18**)	$Zn(Ac)_2$+V_2O_5+en+H_3BO_3+H_2O	Hydrothermal reaction	2	17a
	$[Zn_6V_{10}B_{29}O_{85}]\cdot x$(dien) (**19**)	$NH_4B_5O_{10}\cdot 4H_2O$+NH_4VO_3+H_3BO_3+$Zn(NO_3)_2\cdot 6H_2O$+bapa+H_2O	Hydrothermal reaction	3	14d
$[V_{12}B_{16}]$	$Na[V_{12}B_{16}O_{50}(OH)_7(en)]_2(enH_2)_6(enH)_2(OH)(H_2O)_{19}$ (**20**)	Na_3VO_4+H_3BO_3+$NiCl_2\cdot 6H_2O$+en+H_2O	Hydrothermal reaction	0	16e
	$[H_3O]_2\cdot[H_2en]_3[(VO)_{12}O_4\{B_8O_{17}(OH)_4\}_2\{Na(H_2O)\}_2]\cdot(H_2O)_{6.5}$ (**21**)	H_3BO_3+tat+$VOSO_4$+$CrCl_2$+en	Solvothermal reaction	0	16e
	$[H_3O]_7[Zn_2NaV_{12}B_{16}O_{50}(OH)_8(H_2O)_7]\cdot 4H_2O$ (**22**)	NH_4VO_3+$Zn(Ac)_2\cdot H_2O$+Na_2SO_3+4,4'-bipy+H_2O	Hydrothermal reaction	2	18c
	$[H_3O]_{2.5}[Cd_3Na_{3.5}V_{12}B_{16}O_{50}(OH)_8(H_2O)_8]\cdot 11H_2O$ (**23**)	NH_4VO_3+$Cd(Ac)_2\cdot H_2O$+Na_2SO_3+4,4'-bipy+H_2O	Hydrothermal reaction	2	18c
	$[H_2en]_4\{(VO)_{12}O_4[B_8O_{17}(OH)_4]_2[Mn(H_2O)_2]_2\}$	$(NH_4)_2B_4O_7$+$NaVO_3$+$MnCl_2\cdot 4H_2$	Hydrothermal	2	17c

*Correspounding author. E-mail address: Jianzhou888888@163.com (J. Zhou)

	$\cdot H_2O$ (**24**)	$O+H_2O+en$	reaction		
$[V_{12}B_{17}]$	$[enH][enH_2]_4[(VO)_{12}B_{17}O_{38}(OH)_8]\cdot H_2O$ (**25**)	$B_2O_3+V_2O_3+H_2O+en$	Hydrothermal reaction	0	14b
	$[H_3O]\cdot[H_3teta]_3[V_{12}B_{18}O_{54}(OH)_6(H_2O)]\cdot 5H_2O$ (**26**)	$NH_4VO_3+H_3BO_3+Co+teta+H_2O$	Hydrothermal reaction	0	18a
	$[H_2en]_5\{(VO)_{12}O_6[B_3O_6(OH)_6]\cdot H_2O$ (**27**)	$H_3BO_3+V_2O_5+H_2O+en$	Hydrothermal reaction	0	14b
	$[H_2en]_4H_2[V_{12}B_{18}O_{54}(OH)_6(H_2O)]\cdot 11H_2O$ (**28**)	$NH_4VO_3+(NH_4)_2B_{10}O_{16}\cdot 4H_2O+H_3BO_3+Cu(Ac)_2\cdot H_2O+en+H_2O$	Hydrothermal reaction	0	26
	$[H_2en]_4Na_4H_3[(VO)_{12}O_6B_{18}O_{42}]\cdot 8H_2O$ (**29**)	$V_2O_5+NaOH+B_2O_3+CuCl+H_2O+en$	Hydrothermal reaction	0	27
	$[H_2en]_5[(VO)_{12}O_6B_{18}O_{36}(OH)_6]\cdot 2(H_3O)\cdot 6H_2O$ (**30**)	$NH_4VO_3+H_3BO_3+en+MoO_3+H_2O$	Hydrothermal reaction	0	28
	$[NH_4]_8[1,3\text{-}diapH_2][V_{12}B_{18}O_{60}H_6]\cdot 5H_2O$(**31**)	$V_2O_5+H_3BO_3+1,3\text{-}diap+(NH_4)_2HPO_4+H_2O$	Hydrothermal reaction	0	29
	$K_8(NH_4)_2[V_{12}B_{18}O_{60}H_6]\cdot 18H_2O$(**32**)	$NH_4VO_3+K_2B_4O_7\cdot 4H_2O+H_2O+en$	Hydrothermal reaction	0	29
	$K_{10}[V_{12}B_{18}O_{60}H_6]\cdot 10H_2O$(**33**)	$KVO_3+K_2B_4O_7\cdot 4H_2O+H_2O+en$	Hydrothermal reaction	0	29
	$K_8Cs_2[V_{12}B_{18}O_{60}H_6]\cdot 10.4H_2O$(**34**)	$CsVO_3+K_2B_4O_7\cdot 4H_2O+H_2O+en$	Hydrothermal reaction	0	29
	$[K_5(H_3O)_2]\cdot[(1,3\text{-}diapH_2)]_2[V_{12}B_{18}O_{60}H_6]\cdot 10.8H_2O$ (**35**)	$V_2O_5+H_3BO_3+K_2HPO_4+MnCl_2\cdot 4H_2O+H_2O+1,3\text{-}diap$	Hydrothermal reaction	0	30
	$K_2[H_3O]_7\cdot[enH_2][V_{12}B_{18}O_{60}H_6]\cdot 9H_2O$ (**36**)	$V_2O_5+K_2HPO_4+MnCl_2\cdot 4H_2O+H_2O+en$	Hydrothermal reaction	0	30
	$Li_{10}[V_{12}B_{18}O_{60}H_6]\cdot 28H_2O$(**37**)	$NH_4VO_3+Li_2B_4O_7+H_3BO_3+H_2O$	Hydrothermal reaction	0	31
	$K_4(H_3O)_5[V_{12}B_{18}O_{60}H_6]\cdot 7.5H_2O$(**38**)	$V_2O_5+H_3BO_3+K_2HPO_4+Ni(NO_3)_2\cdot 6H_2O+H_2O+dap$	Hydrothermal reaction	0	32
	$K_9[V_{12}B_{18}O_{60}H_6]\cdot 19.5H_2O$(**39**)	$KVO_3+K_2B_4O_7\cdot 4H_2O+H_2O+toa$	Hydrothermal reaction	0	32
$[V_{12}B_{18}]$	$[H_4tren]_4\cdot[H_3O]\{[Na(H_2O)_4]_3[V_{12}B_{18}O_{54}(OH)_6(H_2O)]_2\}\cdot 41H_2O$ (**40**)	$Na_2SO_3+NH_4VO_3+H_3BO_3+tren+H_2O$	Hydrothermal reaction	0	18d
	$[H_3O]_2\cdot[Na(H_2O)]_2[Na(H_2O)_2]_2[Cu(en)_2][V_{12}B_{18}O_{54}(OH)_6]\cdot 18H_2O$ (**41**)	$VOSO_4+H_3BO_3+CuSO_4\cdot 5H_2O+H_2O+en+H_2C_2O_4\cdot 2H_2O+NaOH$	Hydrothermal reaction	0	33
	$\{K_2V_{12}B_{18}O_{54}(OH)_6(H_2O)[K_8(H_2O)_{16}]\}\cdot 3H_2O$ (**42**)	$NH_4VO_3+H_3BO_3+K_2SO_3+dien+H_2O$	Hydrothermal reaction	0	18i
	$\{K_{10}V_{12}B_{18}O_{54}(OH)_6(H_2O)\}\cdot 14H_2O$ (**43**)	$NH_4VO_3+H_3BO_3+K_2SO_3+dien+Co+H_2O$	Hydrothermal reaction	0	18i
	$[H_2dien]_2\{V_{12}B_{18}O_{54}(OH)_6(H_2O)[K_6(H_2O)_{12}]\}\cdot 3H_2O$ (**44**)	$NH_4VO_3+H_3BO_3+K_2SO_3+Co+dien+H_2O$	Hydrothermal reaction	0	18i
	$K_3Na_5[Hen]_2\{(VO)_{12}O_6[B_3O_6(OH)]_6\}\cdot 13H_2O$ (**45**)	$Na_2B_4O_7+NaVO_3\cdot 2H_2O+KH_2PO_4+en+H_2O$	Hydrothermal reaction	0	34
	$[H_2dap]_2H_6\{(VO)_{12}O_6[B_3O_6(OH)]_6(H_2O)\}\cdot 13H_2O$ (**46**)	$NH_4VO_3+Cu(Ac)_2\cdot H_2O+H_3BO_3+dap+H_2O$	Hydrothermal reaction	0	18e
	$Na_{10}[(H_2O)V_{12}B_{18}O_{60}H_6]\cdot 18H_2O$ (**47**)	$NH_4VO_3+Na_2B_4O_7\cdot 10H_2O+en+H_2O$	Hydrothermal reaction	0	35
	$Na_2[Hen]_4[V_{12}B_{18}O_{60}]\cdot 16H_2O$ (**48**)	$NH_4VO_3+H_3BO_3+ErCl_3+H_2O+tepa+NaOH$	Hydrothermal reaction	0	36
	$[H_2en]_6[V_{12}B_{18}O_{60}]_2\cdot 2tepa\cdot 11H_2O$ (**49**)	$NH_4VO_3+H_3BO_3+ErCl_3+H_2O+tepa+NaOH$	Hydrothermal reaction	0	36
	$[V_{12}B_{18}O_{46}(OH)_{14}(H_2O)_{0.75}]\cdot 20.5H_2O$ (**50**)	$Na_3VO_4\cdot 12H_2O+H_3BO_3+H_2C_2O_4\cdot 2H_2O+Cd(NO_3)_2\cdot 4H_2O+LiOH\cdot H_2O+dien+dap+H_2O$	Hydrothermal reaction	0	37
	$Na_2[V_{12}B_{18}O_{48}(OH)_{12}(H_2O)_{0.5}]\cdot 26.5H_2O$ (**51**)	$Na_3VO_4\cdot 12H_2O+H_3BO_3+LiOH\cdot H_2O+dien+H_2O$	Hydrothermal reaction	0	37
	$[H_3dien]_2\{[Na(H_2O)_3]_4Na_2V_{12}B_{18}O_{56}(OH)_4(H_2O)\}$ (**52**)	$NH_4VO_3+H_3BO_3+Na_2SO_3+dien+H_2O$	Hydrothermal reaction	0	18f
	$K_6[CH_3NH_3]_4[V_{12}B_{18}O_{54}(OH)_6(H_2O)]\cdot 2en\cdot 12$	$NH_4VO_3+K_2B_4O_7\cdot 5H_2O+H_2O+en$	Hydrothermal	0	38

	H_2O (**53**)		reaction		
	$Na_2[enH_2]_4[V_{12}B_{18}O_{54}(OH)_6(H_2O)]\cdot 7H_2O$ (**54**)	$NaOH+V_2O_5+H_3BO_3+en+H_2O$	Hydrothermal reaction	0	39
	$[Zn(en)_2]_6[(VO)_{12}O_6B_{18}O_{39}(OH)_3]\cdot 13H_2O$ (**55**)	$NaVO_3+H_3BO_3+Zn(Ac)_2+en+H_2O$	Hydrothermal reaction	0	[40]
	$[Ni(en)_2]_6[(VO)_{12}O_6B_{18}O_{39}(OH)_3]\cdot 5H_2O$ (**56**)	$Ni(Ac)_2\cdot 4H_2O+V_2O_5+H_3BO_3+H_2O+en$	Hydrothermal reaction	0	[17d]
	$[Ni(en)_2]_6H_2[(VO)_{12}O_6B_{18}O_{42}]\cdot 15H_2O$ (**57**)	$NH_4VO_3+Na_2B_4O_7\cdot 10H_2O+Ni(Ac)_2\cdot 4H_2O+H_2O+en$	Hydrothermal reaction	0	[41]
	$\{[Zn(dien)]_2[Zn(dien)(H_2O)]_4(VO)_{12}O_6[B_3O_6(OH)]_6(H_2O)\}_2\cdot 15H_2O$ (**58**)	$NH_4VO_3+Zn(Ac)_2\cdot 2H_2O+H_3BO_3+dien+H_2O$	Hydrothermal reaction	0	[18e]
	$[Zn(teta)]_6[(VO)_{12}O_6B_{18}O_{36}(OH)_6](H_2O)\cdot 8H_2O$ (**59**)	$V_2O_5 + ZnSO_4\cdot 7H_2O + H_3BO_3 + teta + py + H_2O$	Hydrothermal reaction	0	[18h]
	$Na_8(H_3O)\{[Ni(H_2O)_5][V_{12}B_{18}O_{60}H_6]\}\cdot 12.5H_2O$(**60**)	$NH_4VO_3+Na_2B_4O_7\cdot 10H_2O+Ni(NO_3)_2\cdot 6H_2O+en+H_2O$	Hydrothermal reaction	0	[42]
	$Na_5(H_3O)_4\{[Ni(H_2O)_3(en)][V_{12}B_{18}O_{60}H_6]\}\cdot 9H_2O$(**61**)	$NH_4VO_3+Na_2B_4O_7\cdot 10H_2O+Ni(NO_3)_2\cdot 6H_2O+en+H_2O$	Hydrothermal reaction	0	[42]
	$[Hen][H_2en]\{[Zn(en)_2]_3[V_{12}B_{18}O_{60}H_6]\}\cdot 3H_2O$(**62**)	$NH_4VO_3+H_3BO_3+Zn+en+H_2O$	Hydrothermal reaction	0	[42]
	$Na_9(H_3O)\{Zn_{0.5}[V_{12}B_{18}O_{60}H_6]\}\cdot 11H_2O$(**63**)	$NH_4VO_3+Na_2B_4O_7\cdot 10H_2O+Zn(NO_3)_2\cdot 6H_2O+en+H_2O$	Hydrothermal reaction	1	[42]
	$\{[Zn(dien)(H_2O)]_2V_{12}B_{18}O_{54}(OH)_6\}\cdot x(dien)$ (**64**)	$NH_4B_5O_{10}+NH_4VO_3+H_3BO_3+Zn(NO_3)_2\cdot 6H_2O+dien+H_2O$	Hydrothermal reaction	1	[14c]
	$Na_8[Cu(en)_2]_2[V_{12}B_{18}O_{60}H_6](NO_3)_2\cdot 14.7H_2O$ (**65**)	$NH_4VO_3+Na_2B_4O_7\cdot 10H_2O+Cu(NO_3)_2\cdot 3H_2O +en+H_2O$	Hydrothermal reaction	1	[35]
	$Na_7[Cu(en)_2]_2[V_{12}B_{18}O_{60}H_6](NO_3)\cdot 15.5H_2O$ (**66**)	$NH_4VO_3+Na_2B_4O_7\cdot 10H_2O+Cu(NO_3)_2\cdot 3H_2O +en+H_2O$	Hydrothermal reaction	1	[35]
	$[Zn(H_2teta)_2V_{12}B_{18}O_{54}(OH)_6]\cdot 4H_3O$ (**67**)	$NH_4VO_3+H_3BO_3+ZnO+teta+H_2O$	Hydrothermal reaction	1	[18g]
	$[H_2en]_2\cdot[H_3O][Zn(H_3tepa)V_{12}B_{18}O_{54}(OH)_6]\cdot 3H_2O$ (**68**)	$NH_4VO_3+H_3BO_3+ZnO+tepa+H_2O$	Hydrothermal reaction	1	[18g]
	$Cd_{0.5}\{[Na(H_2O)_2]_2[Na(H_2O)]_2[Na(H_2O)_3]_2V_{12}B_{18}O_{53}(OH)_7(H_2O)_{0.5}\}\cdot 11H_2O$ (**69**)	$Na_3VO_4\cdot 12H_2O+H_3BO_3+CdCl_2\cdot 6H_2O+dap$	Hydrothermal reaction	2	37
	$H_3\{[Cu(en)_2]_5[(VO)_{12}O_6B_{18}O_{42}]\}[B(OH)_3]_2\cdot 16H_2O$ (**70**)	$H_3BO_3+NH_4VO_3+Cu(Ac)_2\cdot H_2O+en+H_2O$	Hydrothermal reaction	2	43
	$\{[Cu(en)_2]_3[Cu(en)_2B(OH)_3]_2[(VO)_{12}O_6(B_{18}O_6(OH)_6)(H_2O)]\}\cdot 13H_2O$ (**71**)	$CuO+NH_4VO_3+Na_2B_4O_7\cdot 10H_2O+H_3BO_3+en+H_2O$	Hydrothermal reaction	3	20a
	$[Cu(en)_2]_4\{Na(H_2O)(\mu\text{-}OH)[B(OH)_2]\}_2[(VO)_{12}O_6(B_{18}O_{36}(OH)_6)]\}\cdot 7H_2O$ (**72**)	$CuO+NH_4VO_3+H_3BO_3+Na_2B_4O_7\cdot 10H_2O+en+H_2O$	Hydrothermal reaction	3	20c
	$[Zn_6(en)_3][(VO)_{12}(B_{18}O_{36}(OH)_6)\cdot(H_2O)]_2\cdot 14H_2O$(**73**)	$NH_4VO_3+(NH_4)_2B_{10}O_{16}\cdot 4H_2O+H_3BO_3+Zn(NO_3)_2\cdot 6H_2O+en+H_2O$	Hydrothermal reaction	3	21
	$[H_3O]_4\{[Cu(dien)(H_2O)]_3V_{12}B_{18}O_{54}(OH)_6(H_2O)\}\cdot 5.5H_2O$ (**74**)	$NH_4VO_3+H_3BO_3+Cu(Ac)_2\cdot H_2O+dien+H_2O$	Hydrothermal reaction	3	18f
	$\{[Zn(H_2O)]_3V_{12}B_{18}O_{54}(OH)_6\}\cdot x(H_2O)$ (**75**)	$NH_4B_5O_{10}+NH_4VO_3+H_3BO_3+Zn(NO_3)_2\cdot 6H_2O+dien+H_2O$	Hydrothermal reaction	3	14c
	$\{[Ni(H_2O)_2]_3V_{12}B_{18}O_{54}(OH)_6\}\cdot x(H_2O)$ (**76**)	$NH_4B_5O_{10}+NH_4VO_3+H_3BO_3+Ni(NO_3)_2\cdot 6H_2O+dien+H_2O$	Hydrothermal reaction	3	14c
	$\{[Mn(H_2O)_2]_3V_{12}B_{18}O_{54}(OH)_6\}\cdot x(H_2O)$ (**77**)	$NH_4B_5O_{10}+NH_4VO_3+H_3BO_3+Mn(NO_3)_2\cdot 6H_2O+dien+H_2O$	Hydrothermal reaction	3	14c
	$[H_3O]_4\{[Cd(H_2O)_2]_3V_{12}B_{18}O_{54}(OH)_6(H_2O)\}\cdot 9.5H_2O$ (**78**)	$NH_4VO_3+H_3BO_3+CdCl_2\cdot 2.5H_2O+dien+H_2O$	Hydrothermal reaction	3	18f
	$[Cd_3(H_2O)_6][(VO)_{12}O_6)(B_{18}O_{36}(OH)_6)]\cdot 10H_2O$ (**79**)	$Cd(NO_3)_2\cdot 4H_2O+NH_4VO_3+H_3BO_3+en+H_2O$	Hydrothermal reaction	3	20b
	$[H_3O]_4\{[Cd(H_2O)_2]_3V_{12}B_{18}O_{54}(OH)_6\}\cdot 26H_2O$ (**80**)	$V(acac)_3+H_3BO_3+Cd(Ac)_2\cdot 2H_2O+ea+H_2O$	Hydrothermal reaction	3	18b
$[V_{12}B_{32}]$	$[H_3O]_{12}[(VO)_{12}\{B_{16}O_{32}(OH)_4\}_2]\cdot 28H_2O$ (**81**)	$BPO_4+NaVO_3+en+H_2O$	Hydrothermal reaction	0	44
	$H_{15}[V_{12}B_{32}O_{84}Na_4]\cdot 13H_2O$ (**82**)	$Na_3VO_4+H_2O+H_3BO_3+MeOH$	Photolysis reaction	0	45

Other［V_xB_y］	$K_2SrVB_5O_{12}$ (**83**)	$KNO_3+SrCO_3+V_2O_5+H_3BO_3$	High temperature solid reaction	2	22b
	$M_3V_2B_{10}O_{23}$[M = Ca (**84a**), Sr (**84b**)]	Ca_2CO_3 (or$SrCO_3$) + V_2O_5 + H_3BO_3	High temperature solid reaction	2	22e
	$Na_3VO_2B_6O_{11}$ (**85**)	$Na_2CO_3+V_2O_5+H_3BO_3$	High temperature solid reaction	3	22c
	Pb_4VBO_8 (**86**)	$PbO+V_2O_5+B_2O_3$	High temperature solid reaction	3	22d
［$V_xB_yP_z$］	$[H_2dabco]_2[VO(HPO_4)_5B_2O]\cdot H_2O\cdot H_3PO_4$(**87**)	$NH_4VO_3+H_3PO_4+ZnCl_2$+dabco+$H_3BO_3+H_2O$	Hydrothermal reaction	0	23a
	$[N_2C_6H_{14}]_2VO(PO_3OH)_4(B_3O_3OH)\cdot 4H_2O$ (**88**)	$V_2O_3+H_3PO_4+H_3BO_3$+DABCO $+H_2O$	Hydrothermal reaction	0	24d
	$[Co(en)_3]_2[V_3P_3BO_{19}][H_2PO_4]\cdot 4H_2O$ (**89**)	$V_2O_5+H_3PO_4+H_3BO_3+CoCl_2\cdot 6H_2O$+en+$H_2O$	Hydrothermal reaction	0	23k
	$[Co(en)_3][H_2en][V_3BP_3O_{19}]\cdot 4.5H_2O$ (**90**)	$VOPO_4\cdot 2H_2O$+$[Co(en)_3]Cl_3+H_2O$	Hydrothermal reaction	0	23b
	$[NH_4]_5[V_3BP_3O_{19}]\cdot H_2O$ (**91**)	$VO_2+H_3PO_4+H_3BO_3+NH_4OH+H_2O+H_2O_2$	Hydrothermal reaction	0	23m
	$[C_4H_{12}N_2]_6[(VO)_2BP_2O_{10}]_4\cdot nH_2O$ (**92**)	$V_2O_3+H_3BO_3+H_3PO_4+H_2O$+pip	Hydrothermal reaction	0	23i
	$Na_{14}[Na\{(VO)_2BP_2O_{10}\}_5]\cdot nH_2O$ (**93**)	$V_2O_3+H_3BO_3+H_3PO_4+Na_2CO_3+H_2O$	Hydrothermal reaction	0	23i
	$[NH_4]_{17}[(NH_4)\{(VO)_2BP_2O_{10}\}_6]\cdot nH_2O_3$ (**94**)	$V_2O_3+H_3BO_3+H_3PO_4+NH_4OH+H_2O$	Hydrothermal reaction	0	23i
	$[H_2en]_2[Na(VO)_{10}\{HO_3POB(O)_2OPO_3H\}_5]\cdot 22.5H_2O$ (**95**)	BPO_4+NaVO_3+en+$FeCl_3\cdot 6H_2O+H_2O$	Hydrothermal reaction	0	23l
	$[NH_4]_2[1,3\text{-}dapH_2]_8[V_2P_2BO_{12}]_6\cdot 15H_2O$ (**96**)	$V_2O_3+H_3BO_3+H_3PO_4+H_2O+NH_4OH$+1,3-dap	Hydrothermal reaction	0	23c
	$H[H_4teta]_4[(NH_4)(VO)_{12}\{O_3POB(O)_2OPO_3\}_6]\cdot 14H_2O$ (**97**)	$H_3BO_3+NH_4VO_3+H_3PO_4$+teta+H_2O	Hydrothermal reaction	0	23e
	$H[H_4teta]_4[K(VO)_{12}\{O_3POB(O)_2OPO_3\}_6]\cdot 16H_2O$ (**98**)	$V_2O_5+H_3BO_3+H_3PO_4$+KCl+teta+H_2O	Hydrothermal reaction	0	23e
	$C_{24}H_{120}B_6N_{17}O_{86}P_{12}V_{12}$ (**99**)	$H_3BO_3+H_3PO_4$+teta+$H_2O+NH_4VO_3$	Hydrothermal reaction	0	23h
	$C_{28}H_{128}B_6KN_{20}O_{84}P_{12}V_{12}$(**100**)	$H_3BO_3+H_3PO_4$+teta+$H_2O+V_2O_5$+KCl	Hydrothermal reaction	0	23h
	$[NH_4]_2[C_2H_{10}N_2]_6[Sr(H_2O)_5]_2[V_2P_2BO_{12}]_6\cdot 10H_2O$(**101**)	$(NH_4)_{18}[V_2P_2BO_{12}]_6\cdot 14H_2O$+$SrCl_2+C_2H_8N_2+HNO_3+H_2O$	Hydrothermal reaction	0	23n
	$[NH_4]_2[C_3H_{12}N_2]_6[Sr(H_2O)_4]_2[V_2P_2BO_{12}]_6\cdot 17H_2O$(**102**)	$(NH_4)_{18}[V_2P_2BO_{12}]_6\cdot 14H_2O$+$SrCl_2+C_2H_8N_2+HNO_3+H_2O$	Hydrothermal reaction	0	23n
	$[NH_4]_3[C_4H_{14}N_2]_{4.5}[Sr(H_2O)_5]_2[Sr(H_2O)_4][V_2P_2BO_{12}]_6\cdot 10H_2O$(**103**)	$(NH_4)_{18}[V_2P_2BO_{12}]_6\cdot 14H_2O$+$SrCl_2+C_2H_8N_2+HNO_3+H_2O$	Hydrothermal reaction	0	23n
	$[Cu_3(Hdien)_6(B_6V_{12}P_{12}O_{72})(H_2O)_{1.98}$(**104**)	$V_2O_3+NH_4B_5O_8\cdot 4H_2O+H_3PO_4$+dien+$H_2O$	Hydrothermal reaction	2	25
	$[imidazolium]_{3.8}\cdot[H_3O]_{1.2}[(VO)_4(BO)_2(PO_4)_5]\cdot 0.3H_2O]$ (**105**)	$V_2O_3+H_3BO_3+H_3PO_4+CuCl_2+N_2C_3H_4+H_2O$	Hydrothermal reaction	2	23j
	$Na_2[VB_3P_2O_{12}(OH)]\cdot 2.92H_2O$ (**106**)	$H_3BO_3+V_2O_5+Na_2HPO_4\cdot 12H_2O$	Boric acid flux method	3	23f
	$[H_2en]_2[(VO)_5(H_2O)\{O_3POB(O)_2OPO_3\}_2]\cdot 1.5H_2O$ (**107**)	BPO_4+NaVO_3+en+$CuCl_2\cdot 2H_2O+H_2O$	Hydrothermal reaction	3	23g

The interaction between the alkali or alkaline-earth metal ion and oxygen atoms of vanadoborates was not considered.

D: dimensionality, 0: molecular, 1: one-dimensional, 2: two-dimensional, 3: three-dimensional.

Ref: Reference.

Abbreviations: en = ethylenediamine, dap = 1,2-diaminopropane, 1,3-dap = 1,3-diaminopropane, $C_2O_4^{2-}$ = oxalic ion, eg = ethylene glycol, dien = diethylenetriamine, teta = triethylenetetramine, tren = tris(2-aminoethyl)amine, tepa = tetraethylenepentamine, peha = pentaethylenehexamine, TBHP = tert-butylhydroperoxide.