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Electronic Supporting Information

New pronounced progress in the synthesis of group 5 polyoxometalates

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compound	Sb-POV – type	conditions	Ref.
$(enH_2)_2\{V_{14}Sb_8O_{42}(H_2O)\}](en) \cdot 4\ H_2O$ (en = ethylenediamine)	α - $V_{14}Sb_8$	4 d, 175 °C	[80]
$\{Ni(phen)_3\}_2[V_{14}Sb_8O_{42}] \cdot phen \cdot 12\ H_2O$ (phen = 1,10-phenanthroline)	α - $V_{14}Sb_8$	7 d, 1 d, 150 °C	[81]
$\{Co(enMe)_3\}_2[V_{14}Sb_8O_{42}(H_2O)]$ (enMe = 1,2-propanediamine)	α - $V_{14}Sb_8$	5 d, 170 °C	[82]
$[\{Zn(en)_2\}_2V_{14}Sb_8O_{42}] \cdot 7\ H_2O$	α - $V_{14}Sb_8$	1 d, 150 °C	[83]
$[H_4V_{14}Sb_8O_{42}(H_2O)] \cdot 5\ H_2O$	β - $V_{14}Sb_8$	5 d, 170 °C	[82]
$(NH_4)_4[V_{14}Sb_8O_{42}] \cdot 2\ H_2O$	β - $V_{14}Sb_8$	14 d, 150 °C	[84]
$(enH_2)_2[V_{14}Sb_8O_{42}(H_2O)] \cdot 3\ H_2O$	β - $V_{14}Sb_8$	7 d, 180 °C	[85]
$(ppzH_2)_2[V_{14}Sb_8O_{42}(H_2O)]$ (ppz = piperazine)	β - $V_{14}Sb_8$	7 d, 180 °C	[85]
$\{Zn_2(dien)_2\}_2[\{Zn(dien)\}_2V_{14}Sb_8O_{42}(H_2O] \cdot 4\ H_2O$ (dien = diethylenetriamine)	β - $V_{14}Sb_8$	7 d, 180 °C	[86]
$[V_{14}Sb_8(aepH)_4O_{42}(H_2O)] \cdot 4\ H_2O$ (aep = 2- piperazine -N-ethylamine)	β - $V_{14}Sb_8$	7 d, 160 °C	[87]
$[\{Ni(en)_2\}_2V_{14}Sb_8O_{42}] \cdot 5.5\ H_2O$	β - $V_{14}Sb_8$	6 d, 180 °C 4 h, 150 °C	[88] [89]
$[\{Co(en)_2\}_2V_{14}Sb_8O_{42}(H_2O)] \cdot 6\ H_2O$	β - $V_{14}Sb_8$	9 d, 160 °C	[90]
$\{Zn(phen)_3\}_2[V_{14}Sb_8O_{42}(H_2O)] \cdot 0.5\ phen \cdot 17\ H_2O$	β - $V_{14}Sb_8$	1 d, 150 °C	[83]
$\{Fe(phen)_3\}_2[V_{14}Sb_8O_{42}(H_2O)] \cdot 11\ H_2O$	β - $V_{14}Sb_8$	1 d, 150 °C	[83]
$\{Ni(cyclen)(en)\}_2[V_{14}Sb_8O_{42}(H_2O)] \cdot ca.10\ H_2O$ (cyclen = 1,4,7,10-tetraazacyclododecane)	α^* - $V_{14}Sb_8$	4 h, 150 °C	[91]
$\{Co(phen)_{2.4}(2,2'\text{-bipy})_{0.6}\}_4[\alpha\text{-}V_{14}Sb_8O_{42}(H_2O)][\beta\text{-}V_{14}Sb_8O_{42}(H_2O)] \cdot 10.5\ H_2O$ (bipy = bipyridine)	α/β - $V_{14}Sb_8$	5 d, 160 °C	[92]
$\{Ni(phen)_3\}_2[V_{14}Sb_5Ge_3O_{42}(OH)_3(H_2O)] \cdot \approx 16\ H_2O$	α - $V_{14}Sb_5Ge_3$	7 d, 150 °C	[93]
$\{Cd(en)_3\}_3[V_{15}Sb_6O_{42}(H_2O)] \cdot 8\ H_2O$	$V_{15}Sb_6$	5 d, 170 °C	[82]
$\{Ni(en)_3\}_2[H_2V_{15}Sb_6O_{42}(H_2O)] \cdot 5\ H_2O$	$V_{15}Sb_6$	5 d, 170 °C	[82]
$\{Co(en)_3\}_2[H_2V_{15}Sb_6O_{42}(H_2O)] \cdot 5\ H_2O$	$V_{15}Sb_6$	5 d, 170 °C	[82]
$(aepH_2)_2[V_{15}Sb_6(aepH)_2O_{42}(H_2O)] \cdot 2.5\ H_2O$	$V_{15}Sb_6$	7 d, 160 °C	[87]
$(trenH_3)_2[V_{15}Sb_6O_{42}] \cdot 0.33\ tren \cdot n\ H_2O$ (tren = tris(2-aminoethyl)amine)	$V_{15}Sb_6$	7 d, 150 °C	[94]
$\{Ni(dien)_2\}_3[V_{15}Sb_6O_{42}(H_2O)] \cdot 12\ H_2O$	$V_{15}Sb_6$	7 d, 150 °C	[95]
$\{Ni(dien)_2\}_3[V_{15}Sb_6O_{42}(H_2O)] \cdot 8\ H_2O$	$V_{15}Sb_6$	7 d, 130 °C	[95]
$\{Co(tren)(H_2O)\}_3[V_{15}Sb_6O_{42}(H_2O)] \cdot H_2O$	$V_{15}Sb_6$	7 d, 170 °C	[96]
$\{Co_2(tren)_3\}_2\{Co(tren)(en)\}[\{V_{15}Sb_6O_{42}(H_2O)(Co(tren)_2)\}V_{15}Sb_6O_{42}(H_2O)] \cdot n\ H_2O$	$V_{15}Sb_6$	7 d, 170 °C	[96]
$\{[Fe(dach)_2]_3[V_{15}Sb_6O_{42}(H_2O)]\} \cdot 8\ H_2O$ (dach = 1,2-diaminocyclohexane)	$V_{15}Sb_6$	7 d, 160 °C	[97]
$\{Co(N_3C_5H_{15})_2\}_2[\{Co(N_3C_5H_{15})_2\}V_{15}Sb_6O_{42}(H_2O)] \cdot 5\ H_2O$ ($N_3C_5H_{15}$ = N-(2-aminoethyl)-1,3-propandiamine)	$V_{15}Sb_6$	7 d, 130 °C	[98]
$\{Ni(N_3C_5H_{15})_2\}_2[\{Ni(N_3C_5H_{15})_2\}V_{15}Sb_6O_{42}(H_2O)] \cdot 8\ H_2O$ ($N_3C_5H_{15}$ = N-(2-aminoethyl)-1,3-propandiamine)	$V_{15}Sb_6$	7 d, 130 °C	[98]
$\{Ni(en)_3\}_3[V_{15}Sb_6O_{42}(H_2O)_x] \cdot n\ H_2O$ ($n \gg 15$)	$V_{15}Sb_6$	7 d, 150 °C	[33]

{Co(en)$_3$}$_3$[V$_{15}$Sb$_6$O$_{42}$(H$_2$O)$_x$] · n H$_2$O (n » 15)	V$_{15}$Sb$_6$	7 d, 150 °C	33
{Fe(en)$_3$}$_3$[V$_{15}$Sb$_6$O$_{42}$(H$_2$O)$_x$] · n H$_2$O (n » 15)	V$_{15}$Sb$_6$	7 d, 150 °C	33
{Ni(en)$_3$}$_3$[V$_{15}$Sb$_6$O$_{42}$(H$_2$O)$_x$] · n H$_2$O (n » 28)	V$_{15}$Sb$_6$	7 d, 150 °C	33
{Ni(trenH)$_2$}[Ni$_2$(tren)$_3$(V$_{15}$Sb$_6$O$_{42}$(H$_2$O)$_{0.5}$] · 2 H$_2$O	V$_{15}$Sb$_6$	5 d, 150 °C	99
{Ni(phen)$_3$}$_2$[{Ni(en)$_2$}V$_{15}$Sb$_6$O$_{42}$(H$_2$O)]·19 H$_2$O	V$_{15}$Sb$_6$	1 d, 150 °C	100
[{Co(teta)$_2$}{Co$_2$(tren)(teta)$_2$}V$_{15}$Sb$_6$O$_{42}$(H$_2$O)] · *ca.*9 H$_2$O (teta = triethylentetraamine)	V$_{15}$Sb$_6$	7 d, 150 °C	101
{Zn(en)$_3$}$_3$ [V$_{15}$Sb$_6$O$_{42}$(H$_2$O)] · 3 en · 10 H$_2$O	V$_{15}$Sb$_6$	5 d, 150 °C	102
{(Zn(en)$_2$(H$_2$O)$_2$)(Zn(en)$_2$)}[{Zn(en)$_2$}V$_{15}$Sb$_6$O$_{42}$(H$_2$O)] · 8.5 H$_2$O	V$_{15}$Sb$_6$	1 d, 150 °C	102
{Zn(phen)$_3$}$_2$[Zn(en)$_2$V$_{15}$Sb$_6$O$_{42}$(H$_2$O)] · 23 H$_2$O	V$_{15}$Sb$_6$	1 d, 150 °C	102
{Ni(dien)$_2$}$_2$[(aepH)$_2$V$_{15}$Sb$_6$O$_{42}$(H$_2$O)]·7.5 H$_2$O	V$_{15}$Sb$_6$	7 d, 150 °C	103
{Ni(en)$_3$}$_3$[V$_{15}$Sb$_2$Ge$_4$O$_{42}$(OH)$_4$(H$_2$O)]·en·≈10 H$_2$O	V$_{15}$Sb$_2$Ge$_4$	7 d, 150 °C	104
{Ni(en)$_3$}$_3$[V$_{15}$Sb$_3$Ge$_3$O$_{42}$(OH)$_3$(H$_2$O)]·≈9 H$_2$O	V$_{15}$Sb$_3$Ge$_3$	7 d, 150 °C	104
{Ni(en)$_3$}$_3$[V$_{15}$Sb$_3$Ge$_3$O$_{42}$(OH)$_3$(H$_2$O)]·≈15 H$_2$O	V$_{15}$Sb$_3$Ge$_3$	1 d, 150 °C	104
{aepH$_2$}$_4$[V$_{16}$Sb$_4$O$_{42}$] · 2 H$_2$O	*α* - V$_{16}$Sb$_4$	7 d, 150 °C	84
[V$_{16}$Sb$_4$O$_{42}$(H$_2$O){VO(dach)$_2$}$_4$]	*α* - V$_{16}$Sb$_4$	7 d, 150 °C	105
{Ni(dien)$_2$}$_4$[V$_{16}$Sb$_4$O$_{42}$(H$_2$O)]	*α* - V$_{16}$Sb$_4$	7 d, 150 °C	106
{Zn$_2$(dien)$_3$}[{Zn(dien)}$_2$V$_{16}$Sb$_4$O$_{42}$(H$_2$O] · 4 H$_2$O	*α* - V$_{16}$Sb$_4$	7 d, 180 °C	86
{[Mn(teta)]$_4$V$_{16}$Sb$_4$O$_{42}$}$_n$ · [(H$_2$O)$_{12}$]$_n$	*α* - V$_{16}$Sb$_4$	5 d, 150 °C	107
{Co(tren)(trenH$_2$)}$_2$[V$_{16}$Sb$_4$O$_{42}$(H$_2$O)] · 6 H$_2$O	*β* - V$_{16}$Sb$_4$	7 d, 130 °C	96
{(trenH$_2$)Zn(tren)}$_2$[V$_{16}$Sb$_4$O$_{42}$(H$_2$O)] · n H$_2$O	*β* - V$_{16}$Sb$_4$	7 d, 130 °C	95