

Supplementary Data for Wu et al.

Synthesis and Characterization of compounds **1-3**.

Synthesis for Compound 1: $[\text{Zn}(\text{en})_2]_2[\text{Zn}(\text{en})\text{H}_2\text{O}]_4[\text{Zn}_4(\text{B}_2\text{O}_4\text{H}_2)(\text{V}_{10}\text{B}_{28}\text{O}_{74}\text{H}_8)(\text{BO}_3\text{H})_2]10\text{H}_2\text{O}$

Method A: 12H₃BO₃(0.75g): 2V₂O₅(0.36g): 4Zn(OAc)₂2H₂O(0.90g): 8en(0.72mL): 200H₂O(3.6mL): 180°C/10days pH=8-9 (pure) large blue crystal, 0.5 x 0.5 x 0.5mm

Method B: 8H₃BO₃(0.50g): 2V₂O₅(0.36g): 3Zn(OAc)₂2H₂O(0.66g) : 6en(0.4mL): 200H₂O(3.6mL): 180°C/10d

Method: The zinc acetate was added to the water, dissolving almost completely. The boric acid and vanadium oxides were then added and solution stirred. Finally the ethylene diamine was added dropwise and the pH tested. The slurry was then heated in 23mL Teflon cup insert of a Parr type pressure vessel under autogenous pressure at 180°C for 10 days. Resulting large blue-green crystals were washed and dried. Typical yield 0.80-0.90g, 60-70% based on V limiting reagent. Method B gave similar results with smaller crystal size ca. 100µm.

Characterization for 1:

pXRD: Top 5 peaks: d, hkl, I/I_{max}: 12.98Å, (101, 011), 100%; 7.13 Å (211, 121), 25%; 4.67 Å, (114), 20%; 10.33 Å (111), 15%; 7.75 Å, (112) 13%.

XPS: elemental ratio (based on Zn =10)
B 26.7 (32); C 34.1 (16); N 16.1 (16); O 68.3 (97); V 7.3 (10); Zn 10.0 (10).
(The number for C and N are typically unreliable due to surface contamination.)

EDAX: elemental ratio from same sample above gave V 13.3 : Zn 10.0.

TGA: 20-200°C	wt loss =	6.5% (calc 7.0% for 14H ₂ O, 4 bound to Zn and 10 lattice H ₂ O)
200-600°C	wt loss =	12.0% (calc 11.9% for 8en plus 6 H ₂ O from the hydroborate)
20-600°C	Total loss =	18.5 % (calc 18.9%)

Synthesis of Compound 2: $\text{K}_6(\text{H}_3\text{O})_8[\text{Mn}_4(\text{C}_2\text{O}_4)(\text{V}_{10}\text{B}_{28}\text{O}_{74}\text{H}_8)(\text{B}_4\text{O}_9\text{H}_2)].24\text{H}_2\text{O}$

15H₃BO₃ (0.90g): V₂O₅ (0.18g): 2KMnO₄ (0.30g): 12en (1mL): 100H₂O (2mL): 140°C/4days, pH= 9 gave 0.35g pale green bars (0.2 x 0.05 x 0.05mm) approx. 50-55% based on V limiting reagent, 70-75% major product, with small dark impurity crystals (25-30% minor product).

Reagents were added and stirred at room temperature for 1h and heated in 23mL Teflon lined autoclave for 4d at 140°C. Product phase purity > 70% was not achieved with modification of conditions. Analysis of small quantities of **2** possible by manual separation of products gave the pXRD, XRF and TGA data below, consistent with the formulation from single crystal X-ray structure analysis.

pXRD: Top 5 peaks: d, hkl, I/I_{max}: 12.75Å, (011), 100%; 3.08Å (151), 5%; 10.68Å, (002), 4%; broad 6.50Å (211, 013) and 6.37 Å (022), 4%; 7.65 Å, (112) 3%.

XRF: elemental ratio based on V = 10 K 6.6 (6); V 10.0 (10); Mn 5.9 (4)

TGA: 20-200°C	wt loss =	12.0 % (calc 13.0% for 24H ₂ O)
200-600°C	wt loss =	12.5.% (calc 11.9% for oxalate and 17 H ₂ O from the H ₃ O and hydroborate)
20-600°C	Total loss =	24.5 % (calc 24.9%)

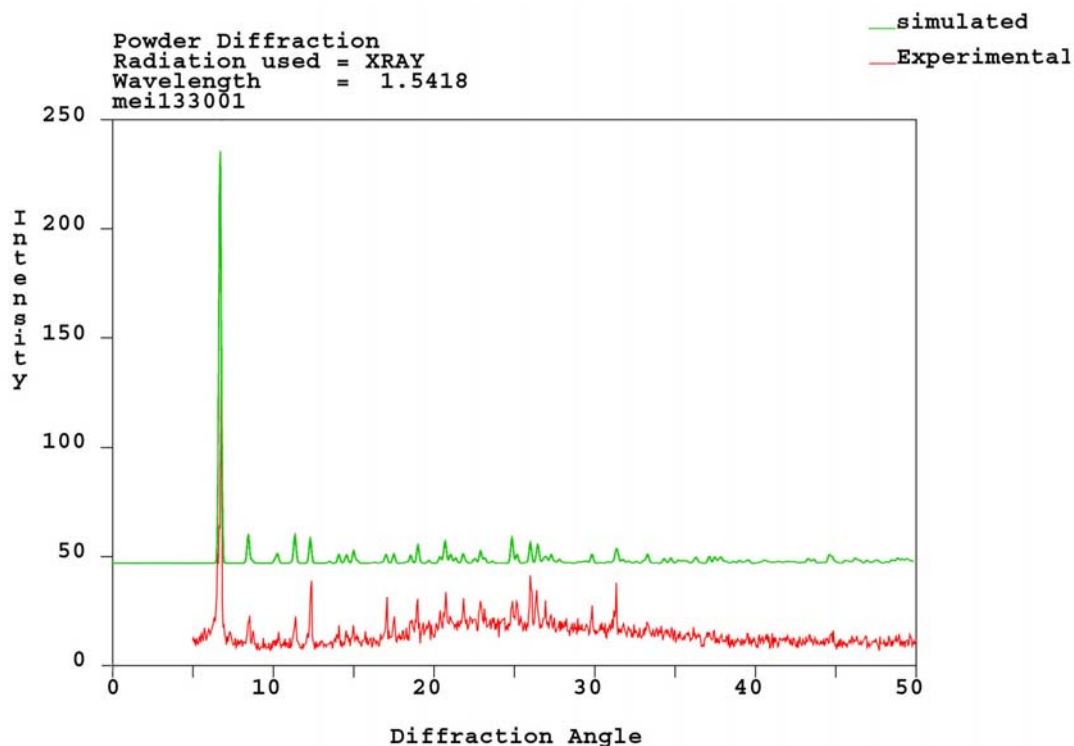
Synthesis of Compound 3:

15H₃BO₃ (0.90g): V₂O₅ (0.18g): 2Mn(OAc)₂2H₂O (0.40g): 5C₂O₄H₂ (0.40g): 15en (1.3mL): 100H₂O (2mL): 110°C/7days, pH = 8.

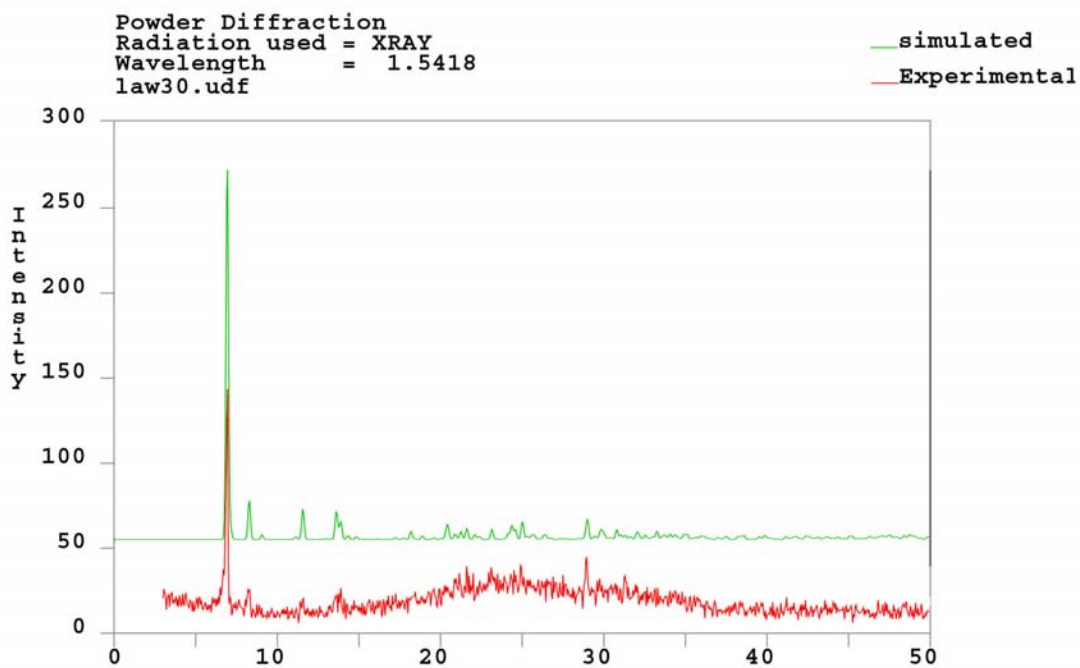
Single crystal structure analysis of **3** was carried out on a small red crystal, further detailed characterization of **3** was not possible since it was only obtained as a minor impurity with [enH₂][Mn₂(C₂O₄)(V₄O₁₂)].

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Experimental and Simulated pXRD patterns for compound 1



Experimental and Simulated pXRD patterns for compound 2

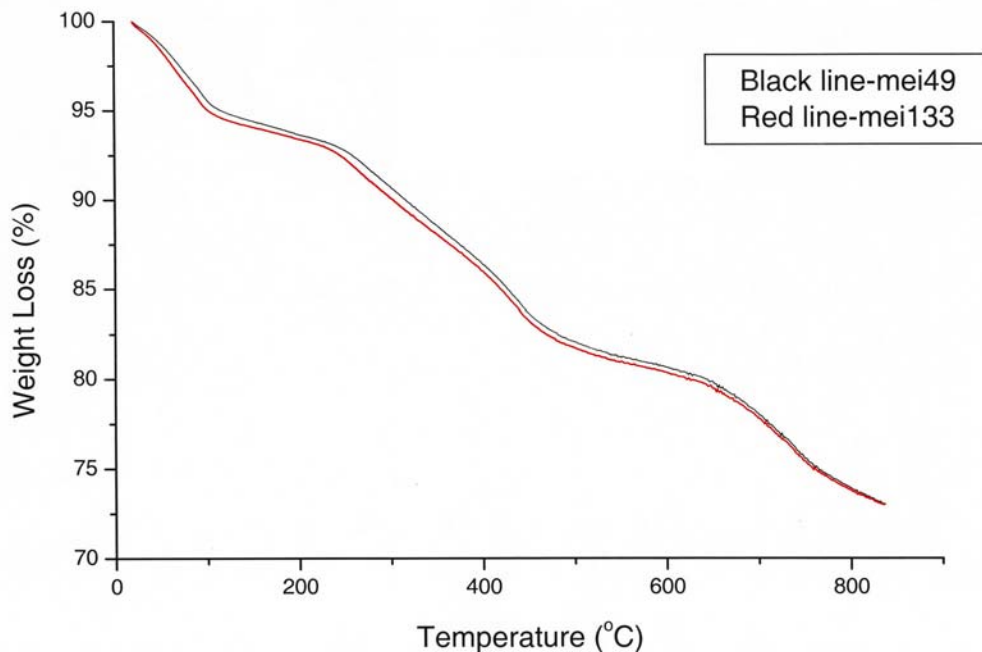


pXRD pattern for 3 not obtained since this is only found as ca. 5% minor product.

Two curves represent measurement on two different samples:

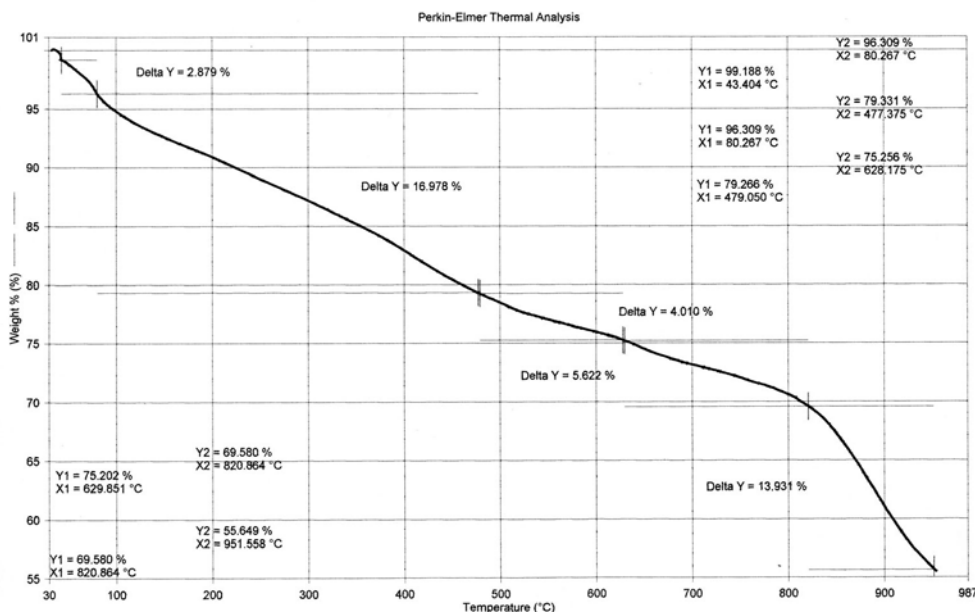
Weight loss from 20-200°C due to H₂O and from 200-500°C due to organic volatiles.

The further weight loss above 600°C is unexpected and awaiting explanation.



Thermal Gravimetric analysis for 2

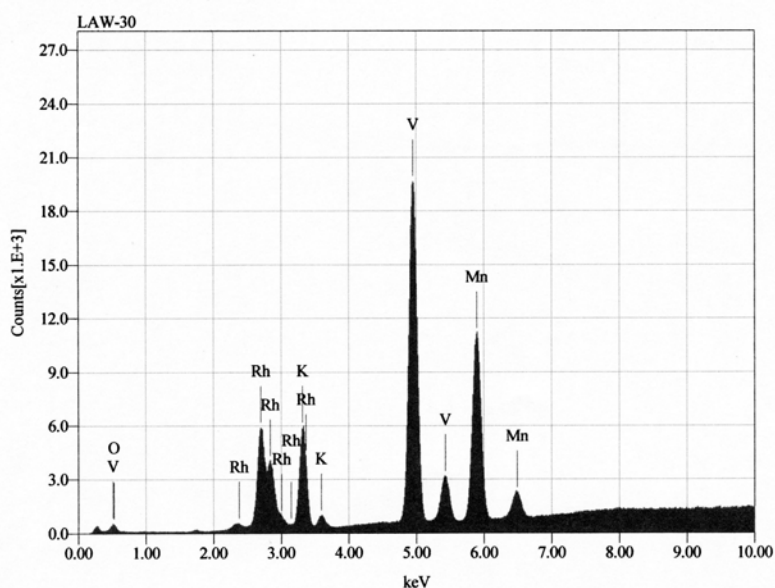
Filename: C:\PE\Pyris1..law30@040813191711.tgd
 Operator ID: herman
 Sample ID: law30
 Sample Weight: 2.023 mg
 Comment: law30



1) Hold for 5.0 min at 30.00°C 2) Heat from 30.00°C to 900.00°C at 5.00°C/min 8/14/04 10:58:27 AM

Print: 2004/9/21 ?? 03:56:38

1/1



File Name: D:\data\Chem\herman\LAW-30.sp2

Sample Name: LAW-30

Date: 2004/8/13 ?? 11:12:17

Acquisition Parameter

Tube Voltage: 30.000 kV Tube Current : 2.200 mA
 Real Time : 1005.13 sec. Dead Time : 45 %
 Live Time : 600.00 sec. Counting Rate: 5016 Counts/sec.
 Preset : Live Time 600.00 sec.
 Energy Range: 0 - 41 keV PHA Mode : Standard
 Pass : VAC

Optical Parameter

Collimator : 4.000 mm Filter : Open

Analysis Elements: O, K, V, Mn, Rh

Fitting Coefficient: 0.1246

Element	Line	Type	Energy	ms%	mol%	K	Net	Error%
8 O	K		0.52	78.6253	91.7732	0.0208335	6461	25.9296
19 K	K		3.31	5.0520	2.4127	0.0090817	79752	0.0287
23 V	K		4.95	9.9624	3.6520	0.0203341	315920	0.0111
25 Mn	K		5.89	6.3604	2.1620	0.0104770	188204	0.0133
45 Rh	L		2.70			0.0600917	121122	

The data from a batch of selected crystals of **2** confirm the stoichiometric presence of potassium, vanadium and manganese in approximate ratios that support of our formulation from the single crystal study. Accurate quantification is hampered in this case by overlap of a Vanadium L-line with Oxygen K- α and interference from the Rh source with potassium K- α . More reliable quantification will also require running of standard samples with the 3 elements K, V and Mn.