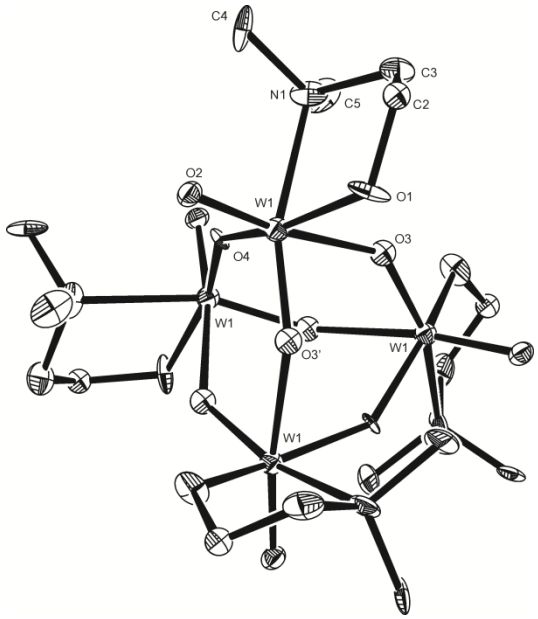
# Supplementary Information

**The structure of $W_4O_4(\mu\text{-}O)_6(dmae)_4$**



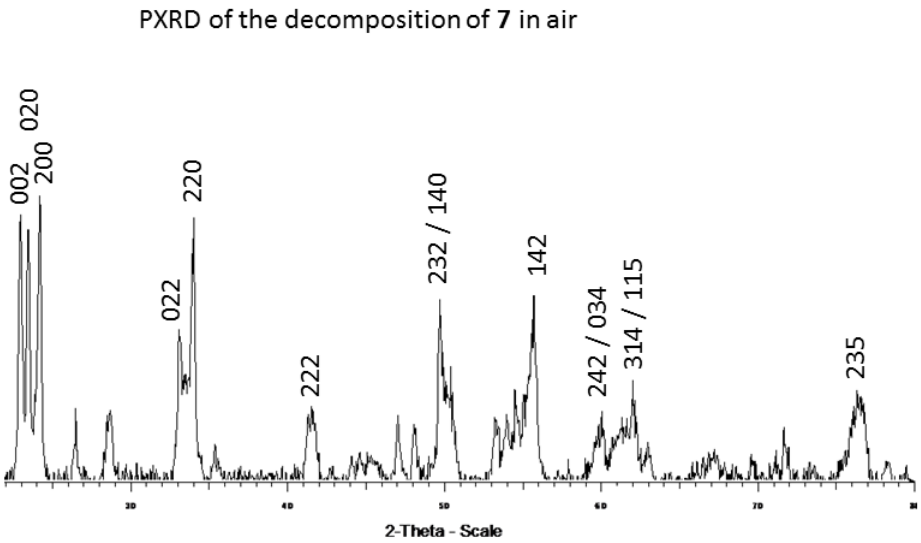

W(1)-O(1) 1.922(8), W(1)-O(2) 1.713(8), W(1)-O(3) 2.269(9), W(1)-O(4) 1.903(4), W(1)-O(3') 1.795(9), W(1)-N 2.387(11) Å; O(2)-W(1)-O(3') 105.1(4), O(4)-W(1)-O(3) 82.1(4), O(2)-W(1)-O(4) 96.2(4), O(1)-W(1)-O(3) 80.3(3), O(3')-W(1)-(4) 98.4(4), O(2)-W(1)-N(1) 93.1(4), O(2)-W(1)-O(1) 97.7(4), O(3')-W(1)-N(1) 161.5(4), O(3')-W(1)-O(1) 98.7(4), O(4)-W(1)-N(1) 82.2(3), O(4)-W(1)-O(1) 154.3(3), O(1)-W(1)-N(1) 75.5(4), O(2)-W(1)-O(3) 170.6(4), O(3)-W(1)-N(1)77.5(4), O(3')-W(1)-O(3) 84.3(3) $^{O}$

Symmetry operation: y-1/2, 1-x, ½-z

**Crystal data for 4**

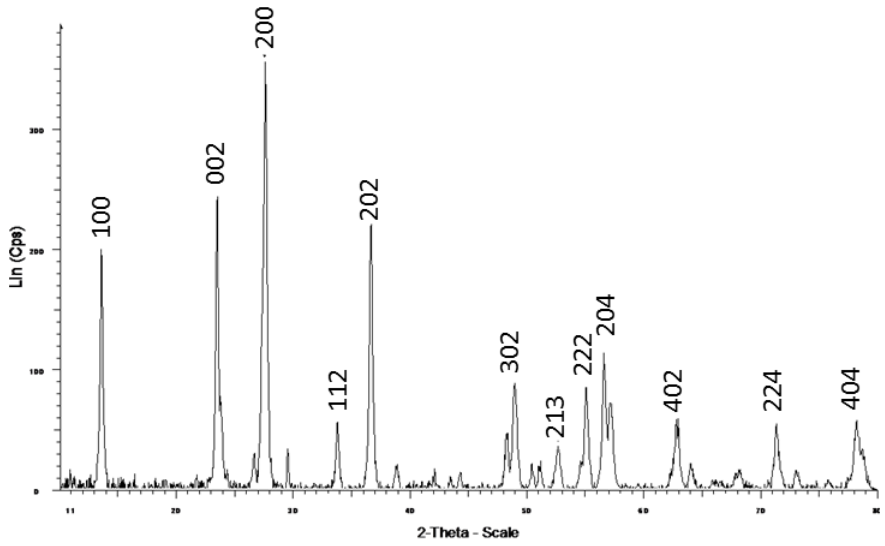
| | | |
|---|---|---|
| Empirical formula | C16 H40 N4 O14 W4 | |
| Formula weight | 1247.92 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Tetragonal | |
| Space group | P42/nbc | |
| Unit cell dimensions | a = 13.4048(19) Å | a= 90°. |
| | b = 13.4048(19) Å | b= 90°. |
| | c = 19.731(4) Å | g = 90°. |
| Volume | 3545.4(10) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 2.338 $Mg/m^3$ | |
| Absorption coefficient | 12.991 $mm^{-1}$ | |
| F(000) | 2288 | |
| Crystal size | 0.10 x 0.10 x 0.02 $mm^3$ | |
| Theta range for data collection | 3.68 to 24.97°. | |
| Index ranges | -15<=h<=15, -11<=k<=11, -23<=l<=23 | |
| Reflections collected | 18139 | |
| Independent reflections | 1556 [R(int) = 0.1599] | |
| Completeness to theta = 24.97° | 99.4 % | |
| Absorption correction | Scalepack | |
| Max. and min. transmission | 0.7812 and 0.3566 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 1556 / 0 / 126 | |
| Goodness-of-fit on $F^2$ | 1.054 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0490, wR2 = 0.1047 | |
| R indices (all data) | R1 = 0.0791, wR2 = 0.1171 | |
| Extinction coefficient | 0.00011(6) | |
| Largest diff. peak and hole | 1.652 and -1.952 $e.Å^{-3}$ | |

A fragment of with a $WO_6$ coordination sphere (12.3% occupancy) was included in the refinement to account for high residual electron density once the atoms of **4** had been located and refined.

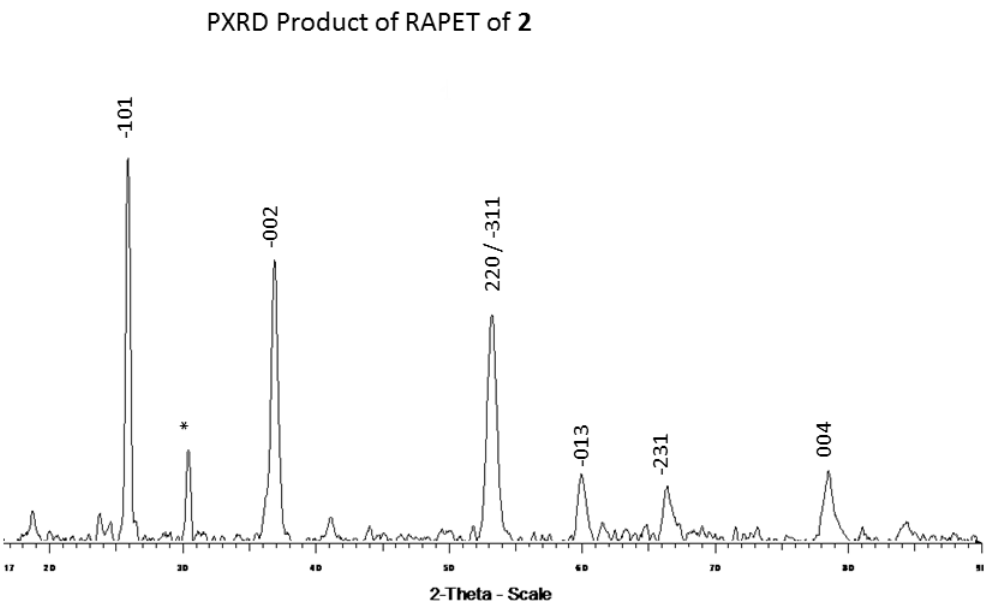



PXRD of the decomposition of **7** in air. Indexing is with reference to orthorhombic $WO_3$ (PDF 89-4480).

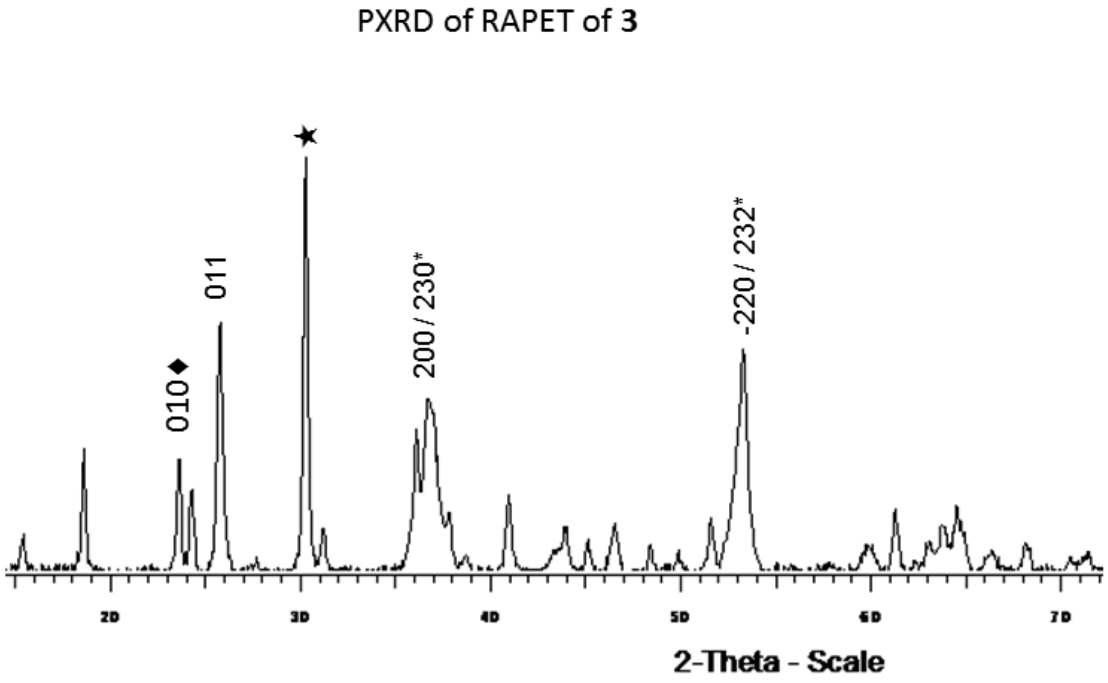
PXRD of the RAPET of **1**




PXRD of the RAPET of 1, indexed to hexagonal $WO_3$ (PDF 85-2160). The (002) line also matches the major line (010) in the pattern for $W_{18}O_{49}$ (PDF 84-1516) and the (202) the major line (111) for $W_2(C,O)$ (PDF 220959)




PXRD of the product from the RAPET of **2**. Lines are indexed to monoclinic $WO_2$ (PDF 32-1393); the peak marked (*) is tentatively assigned to the major diffraction peak of $WO_3.0.5H_2O$ (PDF 36-1143).




PXRD of the product from the RAPET of **3**. Lines are indexed to monoclinic $WO_2$ (PDF 32-1393); lines marked (*,♦,★) are indexed to orthorhombic $WO_2$ (PDF 82-0728), $W_{18}O_{49}$ (PDF 84-1516) and the major diffraction peak of $WO_3.0.5H_2O$ (PDF 36-1143), respectively.