

# Lacunary Tungstotellurates(IV): $[\text{Te}_2\text{W}_{17}\text{O}_{61}]^{12-}$ , $[\text{Te}_2\text{W}_{16}\text{O}_{58}(\text{OH})_2]^{14-}$ and $[\text{Te}_2\text{W}_{18}\text{O}_{62}(\text{OH})_2]^{10-}$

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## Experimental Details

### NMR Spectroscopy

$^{125}\text{Te}$  and  $^{183}\text{W}$  NMR spectra were acquired in o.d. 10 mm sample tubes on a Bruker DRX500 spectrometer equipped with a broadband probe. The  $^{125}\text{Te}$  NMR spectrum was acquired at 158.058 MHz with a spectral width of 100 000 Hz, 3000 transients of 128 K data points and a recycle time of 1.5 to 2 s. The spectrum was processed with a line broadening of 10 Hz. The reference was an external replacement sample of  $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$  with a chemical shift  $\delta$  of 707 ppm versus  $\text{Me}_2\text{Te}$ .<sup>1</sup> The  $^{183}\text{W}$  NMR spectrum was acquired at 20.834 MHz with a spectral width of 6250 Hz, 66 000 transients of 32 K data points and a recycle time of 3.5 to 4 s. The spectrum was processed with a line broadening of 1 Hz. The reference was an external replacement sample of  $\text{Na}_2\text{WO}_4$  (2 M in  $\text{D}_2\text{O}$ ).

### Cyclic and Square Wave Voltammetry

Voltammetric measurements employed an eDAQ ED401 e-corder electroanalysis system equipped with an eDAQ EA161 potentiostat. All measurements used a standard three electrode arrangement with a glassy carbon (1 mm diameter) working electrode, a platinum auxiliary electrode and an aqueous  $\text{Ag}/\text{AgCl}$  (3.4 M  $\text{KCl}$ ) reference electrode. Solutions were 2 mM in analyte with 0.1 M  $\text{KPF}_6$  as supporting electrolyte.

### Powder X-ray Diffraction

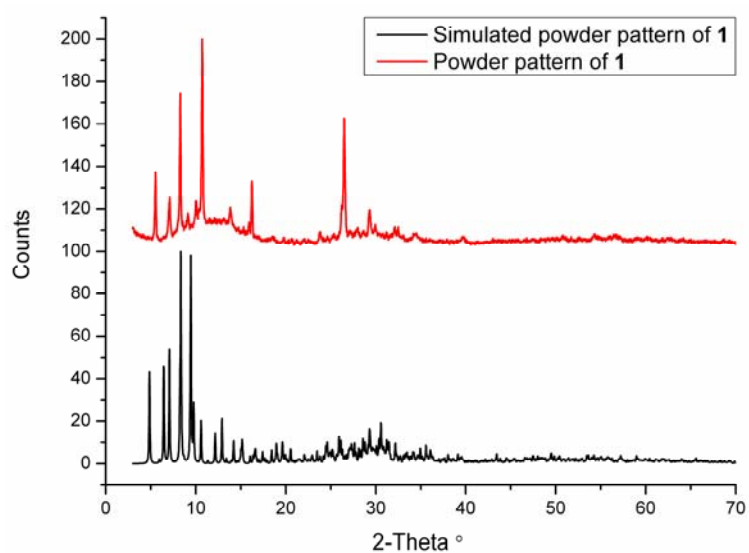
X-ray powder diffraction was carried out on a Bruker B8 ADVANCE diffractometer fitted with a graphite-monochromated  $\text{Cu K}\alpha$  source ( $\lambda = 1.5406 \text{ \AA}$ ) and a scintillation counter detector. The finely-powdered samples were pressed into polycarbonate sample holders and data collected with  $3^\circ < 2\theta < 70^\circ$ , with a step size of  $0.02^\circ$  and a count rate of 2s/step.

### IR Spectroscopy

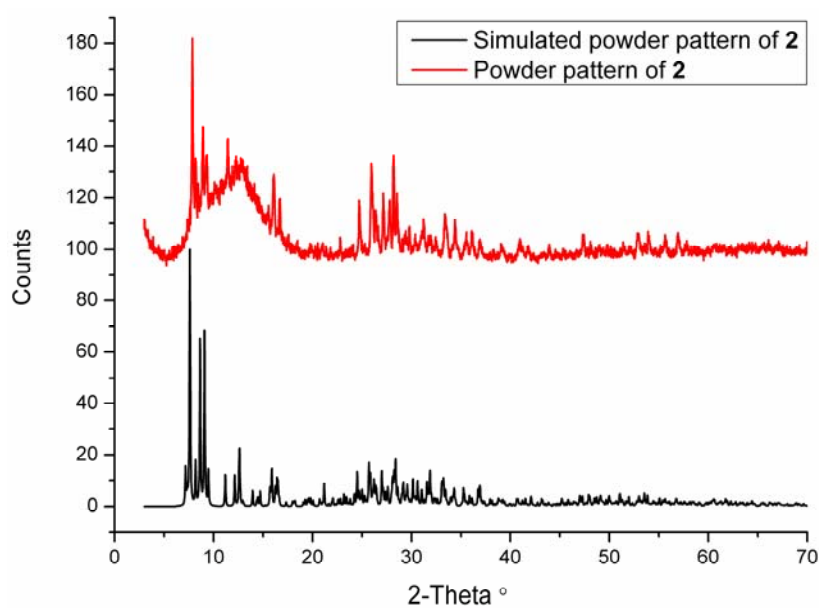
IR spectra were recorded on a Bruker Tensor 27 FTIR spectrometer as pressed KBr disks. Selected IR Data ( $\text{cm}^{-1}$ ) for compound **1**: 1625 (m), 1384 (w), 946 (s), 855 (s), 766 (s), 689 (s), 634 (s), 492 (s), 469 (s); for compound **2**: 1631 (m), 1384 (w), 938 (s), 868 (s), 761 (s), 704 (s), 499 (s).

### Elemental analyses

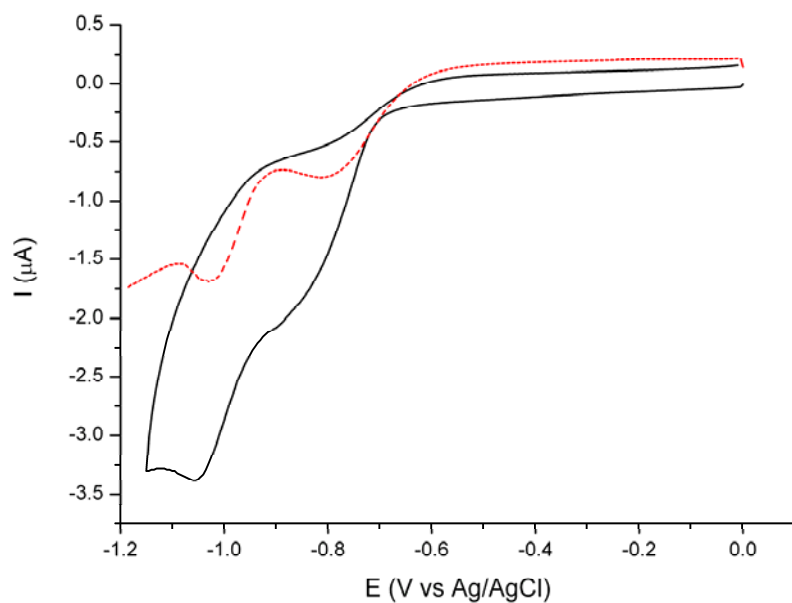
Elemental analyses were performed by the Microanalytical Unit, Research School of Chemistry, Australian National University, Canberra, Australia.



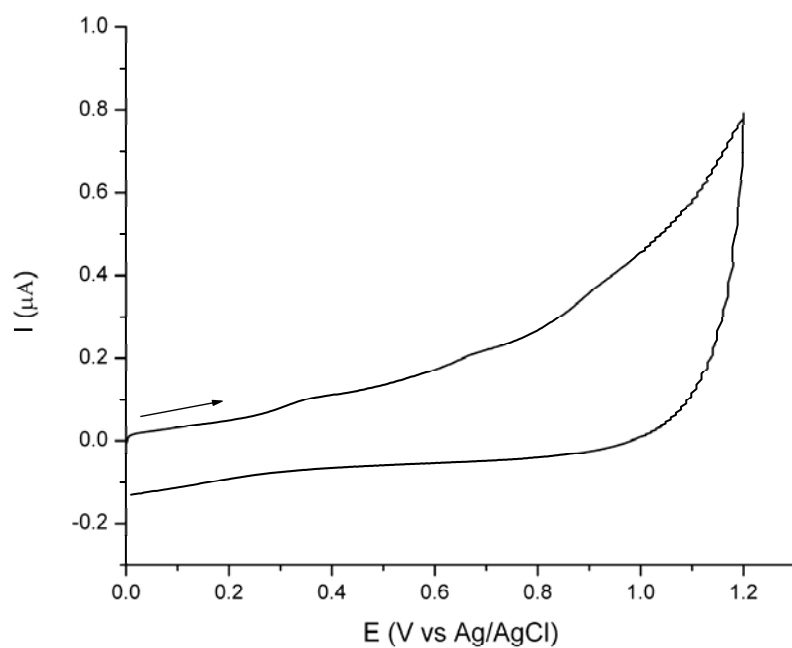
**Fig. S1** Comparison of experimental (top) and simulated (bottom) X-ray diffraction powder patterns for compound **1**.



**Fig. S2** Comparison of experimental (top) and simulated (bottom) X-ray diffraction powder patterns for compound **2**.



**Fig. S3** Cyclic (black, solid line,  $\nu = 100 \text{ mVs}^{-1}$ ) and square wave (red, dashed line,  $f = 15 \text{ Hz}$ ) voltammograms for **1** (2.0 mM in  $\text{H}_2\text{O}$  with 0.1 M  $\text{KPF}_6$ ): cathodic region.



**Fig. S4** Cyclic voltammogram ( $\nu = 100 \text{ mVs}^{-1}$ ) for **1** (2.0 mM in  $\text{H}_2\text{O}$  with 0.1 M  $\text{KPF}_6$ ): anodic region.

### Reference

1. W. Tötsch, P. Peringer and F. Sladky, *J. C. S. Chem. Comm.* 1981, 841.