

# **Supporting Information**

*for*

## **W<sub>2</sub>O<sub>3</sub>I<sub>4</sub> and WO<sub>2</sub>I<sub>2</sub>: Metallic Phases in the Chemical Transport Reaction of Tungsten**

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## Experimental Section

**Synthesis of  $\text{WO}_2\text{I}_2$ :**<sup>1</sup> W,  $\text{WO}_3$  and  $\text{I}_2$  were mixed and pestled in an agate mortar under dry argon atmosphere in a 1 : 2 : 6 molar ratio (100 mg total mass). The reaction mixture was transferred to a silica ampoule (length approx. 15 cm) and fused under vacuum. The silica ampoule was placed in a tube furnace with the reaction mixture in the middle of the tube. The ampoule was heated in a temperature gradient of 800 °C (middle of the tube) to 300 °C at 2 °C/min for 5 h, until cooling to room temperature at 2 °C/min. The crystalline product ( $\text{WO}_2\text{I}_2$ ) was obtained as metallic lustrous needle-shaped plates at the cooler section of the ampoule.

**Synthesis of  $\text{W}_2\text{O}_3\text{I}_4$ :** Ground powder of (50 mg)  $\text{WO}_2\text{I}_2$  was placed in a silica ampoule (length approx. 7 cm) under dry argon atmosphere. The silica ampoule was fused under vacuum and placed into a crucible furnace. The ampoule was heated at 2 °C/min to 380 °C and remained there for 48 h, until cooling to room temperature at 2 °C/min. The compound ( $\text{W}_2\text{O}_3\text{I}_4$ ) was obtained as black needles with metallic luster.

**Computational methods:** Density functional theory calculations were performed with the DFT software package Abinit (v. 9.2.2).<sup>2</sup> The projector-augmented wave (PAW) method<sup>3</sup> was used with the Perdew–Burke–Erzenhof exchange correlation functional<sup>4</sup> and the vdW-DFT-D3 dispersion correction.<sup>5</sup> PAW datasets were used as received from the Abinit repository. Methfessel–Paxton smearing was used to determine the occupation of metallic bands.<sup>6</sup> Plane-wave basis set cutoffs and **k**-point grid spacings were chosen following convergence studies (to 1% in pressure). Structural relaxation was performed prior to calculations of electronic band structures. Example input files are available as Supporting Information.

### **Powder X-ray Diffraction:**

PXRD patterns of well ground powders were recorded using a StadiP diffractometer (Stoe, Darmstadt) with Ge-monochromated  $\text{Cu-K}\alpha_1$  radiation and a Mythen1 Detector.

### **Single-Crystal X-ray Diffraction:**

Single crystals of  $\text{WO}_2\text{I}_2$  and  $\text{W}_2\text{O}_3\text{I}_4$  were collected and placed on the tip of a cryoloop. Data were recorded using a Rigaku XtaLAB Synergy-S single-crystal X-ray diffractometer equipped with HyPix-6000HE detector and monochromated  $\text{Mo-K}\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) at 100 K. The X-ray intensities were corrected for absorption with numerical method using CrysAlisPro 1.171.41.80a (Rigaku Oxford Diffraction, 2021). The structure was solved by direct methods (SHELXS),<sup>7</sup> and full-matrix least-squares structure refinements, performed with SHELXL-2014<sup>8</sup> implemented in Olex2 1.3-ac4.<sup>9</sup>

## Results

**Table S1.** selected Crystal and structure refinement data of  $\text{WO}_2\text{I}_2$  and  $\text{W}_2\text{O}_3\text{I}_4$ , recorded at 100 K.

Empirical formula	$\text{WO}_2\text{I}_2$	$\text{W}_2\text{O}_3\text{I}_4$
CSD No.	2004434	2054404
Formula weight / $\text{g}\cdot\text{mol}^{-1}$	469.65	923.30
Temperature / K	100	100
Wavelength/ pm	71.073	71.073
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Immm</i>	<i>I2/m</i>
<i>a</i> / pm	374.84(3)	924.84(6)
<i>b</i> / pm	390.49(3)	748.82(4)
<i>c</i> / pm	1662.8(1)	1336.48(8)
$\beta/^\circ$		98.810(6)
Volume / $\text{nm}^3$	0.24339(4)	0.91464(10)
Z	2	4
$\mu$ (Mo-K $\alpha$ ) / $\text{mm}^{-1}$	36.26	38.58
Density (calculated) / $\text{g}\cdot\text{cm}^{-3}$	6.41	6.71
Theta range for data collection / $^\circ$	4.90 to 25.93	3.52 to 26.02
Total number of reflections	873	9630
Refined parameters	14	48
$R_1$	0.0181	0.0297
$wR_2$	0.0403	0.0672
Goodness-of-fit on $F^2$	1.071	1.048

**Table S2.** Atomic coordinates, Wyckoff positions (Wyck) and equivalent isotropic displacement parameters (in  $\text{pm}^2 \times 10^{-1}$ ) for  $\text{WO}_2\text{I}_2$ .

atom	Wyck	x	y	z	$U(\text{eq})^a$
W1	2a	1/2	1/2	1/2	39(1)
I1	4i	1/2	1/2	0.66072(4)	12(1)
O1	2d	1/2	0	1/2	6(2)
O2	2b	0	1/2	1/2	18(2)

<sup>a)</sup>  $U(\text{eq})$  is defined as one-third of the trace of the orthogonalized  $U^{ij}$  tensor.

**Table S3.** Atomic coordinates, Wyckoff positions (Wyck) and equivalent isotropic displacement parameters (in  $\text{pm}^2 \times 10^{-1}$ ) for  $\text{W}_2\text{O}_3\text{I}_4$ .

atom	Wyck	x	y	z	$U(\text{eq})^a$
W1	4e	1/4	1/4	1/4	4(1)
W2	4g	1/2	0.2927(1)	1/2	5(1)
I1	4i	0.3420(1)	0	0.5661(1)	7(1)
I2	4i	0.6923(1)	1/2	0.4190(1)	8(1)
I3	8j	0.0142(1)	0.2482(1)	0.3483(1)	9(1)
O1	8j	0.3741(6)	0.2866(7)	0.3761(4)	8(1)
O2	4i	0.2261(10)	1/2	0.2351(7)	18(2)

<sup>a)</sup>  $U(\text{eq})$  is defined as one-third of the trace of the orthogonalized  $U^{ij}$  tensor.

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