Mixed-Metal Monophosphate Tungsten Bronzes Containing Rhodium and Iridium

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Solution combustion synthesis followed by annealing in air led to the MPTB-related phosphates (Rh₁₀W₁₈O₇₈(PO₄)₂₋₄, Ir₁₀W₁₈O₇₈(PO₄)₂₋₄, and Rh₁₀W₁₈O₇₈(PO₄)₂₋₄) (a = 5.258(2) Å, b = 6.538(3) Å, c = 17.322(8) Å, (Rh₁₀/W₁₈O₇₈(PO₄)₂₋₄). Single-crystals of the mixed-metal (Rh,W)-MPTBs at m = 4 and at m = 7 were grown by chemical vapor transport (CVT). Their crystal structures have been refined from X-ray single-crystal data. The crystal structures have been used for the determination of the crystallographic properties of the (Rh,W)-MPTB at m = 4 and m = 7.

Introduction

Thermodynamically metastable, multinary tungsten phosphates with ReO₃-like XRPD-pattern containing platinum group metals have recently been identified as catalyst materials for the formation of maleic anhydride via selective oxidation of n-butane.[1] Annealing these catalyst materials at temperatures above 900°C leads to phases with XRPD pattern resembling those of phosphate tungsten bronzes (PTBs). These mixed-metal PTBs are expected to contain platinum group metals (PGM) in well-established chemical environments, which should lead, following the reasoning of the concepts of single-site catalysts and site isolation,[2] to even better catalyst performance than that observed for the disordered solids with ReO₃-like XRPD-pattern. Furthermore, up to now only a few anhydrous phosphates of rhodium and iridium have been characterized crystallographically (RhPO₄ and RhPO₃)[3] and (IrPO₄)[4]. For this reason further characterization of PGM-containing mixed-metal MPTBs appeared of additional interest.

Since the discovery of the first tungsten bronze A₄WO₉ (A: Na, K) with yellow-golden color and metallic luster by Wöhler in 1825,[5] a wide range of bronzes containing transition metals have been studied.[6] Their structures consist of corner-sharing MO₆ octahedra arranged in a 3D-network, which can be interpreted as a distorted ReO₃-type structure. The interstitial position can be occupied by a large cation A to build a perovskite-type structure, which leads to mixed-valency tungsten (V,VI) and, as a result, interesting physical properties (e.g., electrical conductivity, antiferromagnetic ordering or superconductivity at low temperatures).[7,8] Raveau et al. synthesized phosphate tungsten bronzes (PTB), where ReO₃-like slabs of WO₆ octahedra are separated by phosphate (PO₄) or diphosphate (P₂O₇) groups. These phosphates can be grouped into three classes of PTBs according to their structural features: the monophosphate tungsten bronzes with pentagonal tunnels (MPTB₁) and the general formula (WO₄)₃₋₄(PO₄)₂₋₄ with 2 ≤ m ≤ 14, the monophosphate tungsten bronzes with hexagonal tunnels (MPTB₂) A₄(PO₄)₃(WO₄)₂₋₄ and A₄(WO₄)₃(PO₄)₂₋₄ with 4 ≤ m ≤ 10 and the diphosphate tungsten bronzes (DPTB) A₄(P₂O₇)(WO₄)₂₋₄. For this reason further characterization of PGM-containing mixed-metal MPTBs appeared of additional interest.

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In particular, the MPTB₉ phases with their electronic structure are of interest, because they show phase transitions at low temperatures, which may lead to superconductivity and charge localization effects (charge density waves). An investigation of \((\text{WO}_2)_2(\text{PO}_4)_6\) \((m = 7)\) shows two phase transitions at \(T_1 = 188\ \text{K}\) and \(T_2 = 60\ \text{K}\). These are related to Peierls distortions leading to charge density wave states and superconductivity below \(T < 0.3\ \text{K}\).\(^{[6]}\)

Substitution of tungsten(V) in the \(\text{ReO}_2\)-like slabs by other transition metals is possible. It is already known, that \(\text{WS}^\pm\) can be replaced by appropriate combinations of tungsten(VI) with \(\text{MV}^\pm\) or \(\text{MVI}^\pm\) according to \(\text{M}^{12}\) \(\text{W}^{31}\) and \(\text{M}^{13}\) \(\text{W}^{31}\), respectively. For the MPTB \((\text{WO}_2)_2(\text{PO}_4)_6\) \((m = 2)\) mixed-metal substitution variants with \(\text{M}:\ \text{V}^{11}, \text{Cr}^{31}, \text{Fe}^{21}, \text{Mo}^{51}\) and \(\text{Tl}^{10}\) have been reported.\(^{[10]}\) In addition to the described MPTBs at \(m = 2\), for \(\text{M}:\ \text{Sc}, \text{V}, \text{Cr}, \text{Fe}, \text{Mo}, \text{Ru}, \text{Rh}, \text{In}\) and \text{Ir} the ortho-pyrophosphates \(\text{MV}^\pm(\text{PO}_4)_2\) of identical sum formula (with respect to the MPTBs) but different structure were obtained.\(^{[10]}\)

In this paper we report on synthesis, thermal behavior and characterization of several mixed-metal (Rh,W)- and (Ir,W)-MPTBs. For characterization results from XRPD, SXRD, electron microscopy, UV/vis-spectroscopy, and magnetic measurements are presented.

**Results and Discussion**

**Synthesis**

The new mixed-metal (mm) MPTBs \((\text{Rh}_{1/2}\text{W}_{5/6}\text{O}_{10}\text{S})_2(\text{PO}_4)_6\) \((\text{Rh}_{1/2}\text{W}_{3/4}\text{O}_{10}\text{S})_2(\text{PO}_4)_6\) \((\text{Rh}_{2/3}\text{W}_{1/2}\text{O}_{10}\text{S})_2(\text{PO}_4)_6\) have been obtained as single-phase, micro-crystalline powders (XRPD) by solution combustion synthesis (SCS)\(^{[11]}\) followed by annealing of the combustion products in air. For SCS \(\text{Rh(NO}_3)_4\) \((\text{Umicore, Hanau})\) or \(\text{Ir(acac)}_3\) \((\text{Umicore, Hanau})\), \((\text{NH}_4)_2\text{W}_{1/2}\text{O}_{4/3}\) \((\text{H}_2\text{O})_8\) \((\text{Alfa Aesar, Karlsruhe})\), \text{H}_2\text{PO}_4\) \((\text{WWR, Darmstadt})\), and the polydentate ligand glycine \((\text{Labochem International, Heidelberg})\) were dissolved in water \((\text{molar ratio metal : glycine = 1:3})\). Conc. \text{HNO}_3 \((\text{Fisher Scientific, Schwerte})\) in excess was added as oxidant to the solution to prevent the reduction of rhodium or iridium during the combustion. To our observation, formation of the PGM metals is irreversible under the described reaction conditions and has to be avoided. The solutions were evaporated at temperatures \(\vartheta = 100\ \text{°C}\) and thereafter ignited in a preheated furnace at \(\vartheta = 400\ \text{°C}\), where a self-propagating combustion took place and yielded black, voluminous, amorphous (XRPD) powders. These intermediates were ground and annealed in air with stepwise rising of the temperature up to \(1000\ \text{°C}\) for \((\text{Rh}_{1/2}\text{W}_{5/6}\text{O}_{10}\text{S})_2(\text{PO}_4)_6\) and \((\text{Ir}_{1/2}\text{W}_{5/6}\text{O}_{10}\text{S})_2(\text{PO}_4)_6\) and up to \(1100\ \text{°C}\) for \((\text{Rh}_{2/3}\text{W}_{1/2}\text{O}_{10}\text{S})_2(\text{PO}_4)_6\) and \((\text{Rh}_{2/3}\text{W}_{1/2}\text{O}_{10}\text{S})_2(\text{PO}_4)_6\). Thus obtained powders display a dark-green color for the rhodium and black for the iridium compounds. XRPD pattern were recorded after each annealing step to control the progress of product formation until the thermodynamically stable mm-MPTB phase was obtained single-phase (see XRPD pattern in Figure 1 and Figures S1-S4). In case of \((\text{Rh}_{1/2}\text{W}_{5/6}\text{O}_{10}\text{S})_2(\text{PO}_4)_6\) the described procedure led always to \((\text{Rh}_{2/3}\text{W}_{1/2}\text{O}_{10}\text{S})_2(\text{PO}_4)_6\) as minor by-phase. We attribute this outcome to the close proximity of chemical composition of the two compounds and the rather small amounts of material used for synthesis, due to the high cost of rhodium.

Experiments aiming at \((\text{Rh}_{2/3}\text{W}_{1/2}\text{O}_{10}\text{S})_2(\text{PO}_4)_6\) \((m = 3)\), \((\text{Rh}_{2/3}\text{W}_{1/2}\text{O}_{10}\text{S})_2(\text{PO}_4)_6\) \((m = 5)\) or \((\text{Rh}_{2/3}\text{W}_{1/2}\text{O}_{10}\text{S})_2(\text{PO}_4)_6\) \((m = 8)\) led to the neighboring MPTB phases. In case of iridium only \((\text{Ir}_{1/2}\text{W}_{5/6}\text{O}_{10}\text{S})_2(\text{PO}_4)_6\) was formed. The mixed-metal MPTBs \((\text{M}_{1/2}\text{W}_{1/2}\text{O}_{10}\text{S})_2(\text{PO}_4)_6\) \((m = 2)\) with \(\text{M} = \text{Rh}, \text{Ir}\) were never observed. Instead, formation of \(\text{M}(\text{WO}_2)_2(\text{PO}_4)_3\) \((\text{M} = \text{Rh}, \text{Ir})\) did occur, as previously described by Roy et al.\(^{[12]}\)

![Figure 1](https://example.com/figure1.png)

**Figure 1.** XRPD pattern (IP Guinier technique, Cu-Kα) of \((\text{Rh}_{1/2}\text{W}_{5/6}\text{O}_{10}\text{S})_2(\text{PO}_4)_6\) (top) and \((\text{Ir}_{1/2}\text{W}_{5/6}\text{O}_{10}\text{S})_2(\text{PO}_4)_6\) (bottom) with simulations based on SXRD data. \((\text{Ir}_{1/2}\text{W}_{5/6}\text{O}_{10}\text{S})_2(\text{PO}_4)_6\) (middle) with a simulation based on \((\text{Rh}_{2/3}\text{W}_{1/2}\text{O}_{10}\text{S})_2(\text{PO}_4)_6\) (grey) and \((\text{WO}_2)_2(\text{PO}_4)_6\) \((\text{black})\) with an even distribution of rhodium/iridium over all three tungsten sites.

Lattice parameters of the MPTBs were determined using the program SOS\(^{[11]}\) and \(\alpha\)-SiO₂ \((\text{Merck, Darmstadt})\) as internal standard (see Table 1). Interestingly, the lattice parameters \(a\) and \(b\) which are parallel to the \(\text{ReO}_2\)-type slabs of the (Rh,W)-MPTBs are smaller compared to the pure tungsten MPTBs, whereas the parameter \(c\) (perpendicular to the \(\text{ReO}_2\)-type slabs) is enlarged (Table 1).

![Figure S1](https://example.com/figureS1.png)

**Table 1.** Lattice parameters of the MPTBs

| Compound                | \(a\) (Å) | \(b\) (Å) | \(c\) (Å) |
|-------------------------|-----------|-----------|-----------|
| \((\text{Rh}_{1/2}\text{W}_{5/6}\text{O}_{10}\text{S})_2(\text{PO}_4)_6\) |          |           |           |
| \((\text{Ir}_{1/2}\text{W}_{5/6}\text{O}_{10}\text{S})_2(\text{PO}_4)_6\) |          |           |           |
| \((\text{Rh}_{2/3}\text{W}_{1/2}\text{O}_{10}\text{S})_2(\text{PO}_4)_6\) |          |           |           |
| \((\text{Ir}_{2/3}\text{W}_{1/2}\text{O}_{10}\text{S})_2(\text{PO}_4)_6\) |          |           |           |

![Figure S1](https://example.com/figureS1.png)

**Figure S1.** Lattice parameters of the MPTBs.
Progress of phase formation and thermal decomposition

For \((\text{Rh}_{12} \text{W}_{19/2} \text{O}_{14})_4 \text{(PO}_4)_4\) the \((\text{Rh}, \text{W})\)-MPTB at \(m = 7\), as representative example, the progress of phase formation starting from the amorphous intermediate obtained by SCS is summarized in Figure 2. It shows, rather unexpectedly, strong kinetic effects during phase formation. After SCS \(400 \degree C\) ignition temperature; hot spot temperature up to \(900 \degree C\) for a few seconds) the intermediate exhibits a diffraction pattern typical of an amorphous solid. Heating to \(750 \degree C\) leads to less “amorphous background” and development of rather broad Bragg peaks indicating the formation of a thermodynamically metastable phase with a \(\text{ReO}_3\)-related pattern. The chemical composition of this phase, \((\text{Rh}_{12} \text{W}_{19/2} \text{O}_{14})_4 \text{(PO}_4)_4\) can be re-written as \((\text{Rh}_{12/2/2} \text{W}_{19/2} \text{P}_{19/20} \text{O}_{79/20})_4\) to emphasize its relation to \(\text{ReO}_3\) and to show the oxygen-deficiency as a consequence of the average oxidation state of the cations. This and related \(\text{ReO}_3\)-like phases are obtained with high reproducibility by the described protocol and they show remarkable thermal stability against transformation into the thermodynamically stable equilibrium phases. However, without SCS and initial annealing temperatures too high these phases were never obtained.

Surprisingly, transformation (equilibration) of the single-phase homogenous \(\text{ReO}_3\)-like phase to the microcrystalline powder of \((\text{Rh}_{12} \text{W}_{19/2} \text{O}_{14})_4 \text{(PO}_4)_4\) \((m = 7)\) does not occur directly, but via the apparently kinetically favorable formation of the \((\text{Rh}, \text{W})\)-MPTB at \(m = 4\) (depleted in \(\text{WO}_3\) with respect to the starting composition) and a \(\text{WO}_3\)-rich phase with \(\text{ReO}_3\)-related XRPD pattern. Thus, as can be taken from Figure 2, above \(800 \degree C\) a pattern similar to \((\text{WO}_3)_4 \text{(PO}_4)_4\) \((\text{MPTB at } m = 4)\) begins to emerge from the amorphous background. Simultaneously, the lattice parameter \(a\) of the \(\text{ReO}_3\)-like phase shrinks slightly from \(3.79 \text{\textbar} 3.71 \text{\textbar} \text{Å}\) (see Table 2) and is thus approaching the value given in literature for cubic \(\text{WO}_3\). We are therefore relating this change to a depletion of the \(\text{ReO}_3\)-like phase of rhodium and phosphorus and an enrichment by \(\text{WO}_3\). The powder obtained after annealing at \(1000 \degree C\) (Figure 2) clearly shows, according to its XRPD pattern, an off-equilibrium mixture of three phases. The presence of the \(\text{WO}_3\)-rich, \(\text{ReO}_3\)-like phase \((\sim 16 \% \text{wt})\) and of the intermediate \((\text{Rh}, \text{W})\)-MPTB \((m = 4; \sim 47 \% \text{wt})\), which has a higher content of rhodium and phosphorus than the starting mixture is apparently kinetically controlled. The equilibrium phase \((\text{Rh}_{12} \text{W}_{19/2} \text{O}_{14})_4 \text{(PO}_4)_4\) \((m = 7)\) is already present in the mixture at \(\sim 37 \% \text{wt}\). Eventually, after annealing at \(1100 \degree C\) the targeted \((\text{Rh}, \text{W})\)-MPTB at \(m = 7\) is obtained as single-phase powder. Further heating up to \(1200 \degree C\) of this \((\text{Rh}, \text{W})\)-MPTB in air leads to decomposition to \(\text{P}_2\text{O}_5\) vapor, \(\text{WO}_3\) (monoclinic after quenching to ambient temper-

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**Table 1. Lattice parameters from XRPD data of (Rh,W)- and (Ir,W)-MPTBs in comparison to the pure tungsten phosphates.**

| Compound | \(a\) [Å] | \(b\) [Å] | \(c\) [Å] | \(\beta\) [°] |
|----------|-----------|-----------|-----------|-----------|
| \((\text{RhO}_3)_4 \text{(PO}_4)_4\) \(^{[14]}\) | 5.285(2) | 6.569(1) | 17.351(3) |
| \((\text{Rh}_{12} \text{W}_{19/2} \text{O}_{14})_4 \text{(PO}_4)_4\) | 5.223(1) | 6.513(2) | 17.356(6) |
| \((\text{Rh}_{12} \text{W}_{19/2} \text{O}_{14})_4 \text{(PO}_4)_4\) \(^{[15]}\) | 5.2232(7) | 6.5604(7) | 23.549(3) |
| \((\text{IrO}_3)_4 \text{(PO}_4)_4\) \(^{[16]}\) | 5.2927(7) | 6.5604(7) | 23.599(7) |
| \((\text{WO}_3)_4 \text{(PO}_4)_4\) \(^{[17]}\) | 5.2927(7) | 6.5604(7) | 23.549(3) |
| \((\text{Rh}_{12} \text{W}_{19/2} \text{O}_{14})_4 \text{(PO}_4)_4\) \(^{[18]}\) | 5.229(2) | 6.540(3) | 23.599(7) |
| \((\text{Rh}_{12} \text{W}_{19/2} \text{O}_{14})_4 \text{(PO}_4)_4\) \(^{[19]}\) | 5.229(1) | 6.557(2) | 26.654(8) |
| \((\text{Rh}_{12} \text{W}_{19/2} \text{O}_{14})_4 \text{(PO}_4)_4\) \(^{[20]}\) | 5.245(2) | 6.507(2) | 26.693(8) |
| \((\text{Rh}_{12} \text{W}_{19/2} \text{O}_{14})_4 \text{(PO}_4)_4\) \(^{[21]}\) | 5.2510(4) | 6.4949(5) | 26.6854(19) |
| \((\text{Rh}_{12} \text{W}_{19/2} \text{O}_{14})_4 \text{(PO}_4)_4\) \(^{[22]}\) | 5.2510(4) | 6.4949(5) | 26.6854(19) |

[a] Lattice parameters from single-crystal measurement at room temperature (crystals from CVT, composition from structure refinement).

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**Figure 2.** XRPD pattern (Guinier technique, Cu-K \(_\alpha\)) of \((\text{Rh}_{12} \text{W}_{19/2} \text{O}_{14})_4 \text{(PO}_4)_4\) after several consecutive steps of annealing starting with the combustion product from SCS, rel. amounts (wt %) estimated with MATCH!\(^{[10]}\)
nature), and rhodium (see Eq. 1). The latter two solid phases were identified by XRPD.

The progress of phase formation observed for the other mm-MPTBs under consideration, (Rh$_{1/2}$W$_{1/2}$O$_{3}$)(PO$_{4}$)$_{4}$ (Ir$_{1/2}$W$_{1/2}$O$_{3}$)(PO$_{4}$)$_{4}$, and (Rh$_{1/2}$W$_{1/2}$O$_{3}$)(PO$_{4}$)$_{4}$ is very similar to the one described for (Rh$_{2/21}$W$_{19/21}$O$_{4}$)$_{4}$ (see Tables S5-S7). However, there is variation in the temperature required to obtain the single-phase mm-MPTB and in their decomposition temperatures. Single-phase powders of (Rh$_{1/6}$W$_{5/6}$O$_{3}$)(PO$_{4}$)$_{4}$ and (Ir$_{1/6}$W$_{5/6}$O$_{3}$)(PO$_{4}$)$_{4}$ (both $m = 6$) are formed at about 800°C, (Rh$_{1/9}$W$_{8/9}$O$_{3}$)(PO$_{4}$)$_{4}$ (m = 7) around 1050°C and (Rh$_{2/21}$W$_{19/21}$O$_{4}$)$_{4}$ (m = 7) around 1100°C. Short annealing periods of a few hours only slightly above their decomposition temperatures lead to stepwise loss of P$_{2}$O$_{5}$ and the formation of elementary rhodium and the (Rh,W)-MPTB with the next higher rhodium/P molar ratio. Overall, the decomposition temperature of the (Rh,W)-MPTBs increases with decreasing content of rhodium/P$_{2}$O$_{5}$. This observation fits to the decomposition behavior of pure rhodium phosphates (Rh(PO$_{4}$)$_{3}$, RHPO$_{4}$), where the activity of P$_{2}$O$_{5}$ is higher and decomposition in air begins at 950°C.[18,19]

\[
3 \text{(Rh}_{2/21}\text{W}_{19/21}\text{O}_{4}\text{)}_4 \text{PO}_4(s) \rightarrow \text{38 WO}_3(s) + 4 \text{Rh(s)} + 3 \text{P}_2\text{O}_5(g) + 3 \text{O}_2(g) \quad (1)
\]

Based on their thermal decomposition temperatures and the assumption that $p$(O$_2$) should exceed 0.2 bar for a detectable decomposition effect, an estimate of the thermodynamic data $\Delta_\text{f}H^{\circ}_{298}$, $S^\circ_{298}$, $C_p$ (coefficients A, B, C) of (Rh$_{1/6}$W$_{5/6}$O$_{3}$)(PO$_{4}$)$_{4}$ and (Rh$_{2/21}$W$_{19/21}$O$_{4}$)$_{4}$ was possible using the data of the binary oxides WO$_{3}$, Rh$_2$O$_3$, and P$_2$O$_{5}$. The estimation follows a procedure applied by Schäfer for LaPO$_4$.[20] For a summary of thermodynamic data used in the context of this paper, see Table S1.

Crystallization by chemical vapor transport

Crystals of the (Rh,W)-MPTBs (Rh$_{1/6}$W$_{5/6}$O$_{3}$)(PO$_{4}$)$_{4}$ (m = 4), (Rh$_{1/9}$W$_{8/9}$O$_{3}$)(PO$_{4}$)$_{4}$ (m = 6), and (Rh$_{2/21}$W$_{19/21}$O$_{4}$)$_{4}$ (m = 7) have been grown by chemical vapor transport (CVT)[21] in sealed silica tubes (I = 14 cm, d = 1.5 cm) with chlorine as transport agent. These show a dark greenish color, have edge lengths up to 300 µm and are isometric with a rectangular shape (Figure 3).

Pre-synthesized, single-phase powders (from SCS followed by annealing in air) were used as starting materials for CVT. Small amounts of PtCl$_3$ (~15 mg) were added for in situ generation of chlorine, the transport agent. Temperature gradients 950 → 900°C for (Rh$_{1/6}$W$_{5/6}$O$_{3}$)(PO$_{4}$)$_{4}$ and 1090 → 1050°C for (Rh$_{1/9}$W$_{8/9}$O$_{3}$)(PO$_{4}$)$_{4}$ and (Rh$_{2/21}$W$_{19/21}$O$_{4}$)$_{4}$ were applied. Ampoules were kept in the furnaces for 14 d. Under the given experimental conditions no decomposition of the (Rh,W)-MPTBs was observed. However, transport of (Rh$_{1/6}$W$_{5/6}$O$_{3}$)(PO$_{4}$)$_{4}$ and (Rh$_{2/21}$W$_{19/21}$O$_{4}$)$_{4}$ in the temperature gradient 950 → 900°C led to deposition of (Rh$_{1/9}$W$_{8/9}$O$_{3}$)(PO$_{4}$)$_{4}$ in the sink due to non-stationary behavior of the system. For a general explanation of non-stationary transport behavior see.[21,22]

Chemical vapor transport of (Rh$_{1/6}$W$_{5/6}$O$_{3}$)(PO$_{4}$)$_{4}$ with chlorine as transport agent was modelled with the computer program CVTrans[23] using thermodynamic data given in Table S1. According to the modelling and in agreement with literature on CVT of WO$_3$ and Rh$_2$O$_3$, the transport active gas species are WO$_3$Cl$_2$, RhCl$_3$, P$_2$O$_{5}$, and O$_2$ (see Eq. 2).[18,21]

\[
\text{(Rh}_{1/6}\text{W}_{5/6}\text{O}_3\text{)}_4\text{(PO}_4\text{)}_4(s) + 13/12 \text{Cl}_2(g) \rightarrow

\text{1/6 RhCl}_3(g) + 5/6 \text{WO}_3\text{Cl}_2(g) + \text{P}_2\text{O}_5(g) + 13/24 \text{O}_2(g) \quad (2)
\]

Crystal structure analyses

The (Rh,W)-MPTB at $m = 4$ and $m = 7$ are isotypic to their pure tungsten MPTB counterparts (WO$_{3}$)$_{4}$ (P2$_1$/2, Z = 1) and (WO$_{3}$)$_{4}$ (P2$_1$/n, Z = 1). Table 3 provides a summary on data collection and refinement of the crystal structures. Atomic coordinates and isotropic displacement parameters are shown in Table 4 and Table 5 (Anisotropic displacement parameters see Table S2 and Table S3). Refinements for both (Rh,W)-MPTBs were hampered by twinning, cation disorder, and possibly stacking faults all of which are typical for monophosphate tungsten bronzes as has been pointed out in literature several times.[25] Due to the limited quality of the refinements we refrain from discussing interatomic distances (see Figures S8 and S9) in detail. Nevertheless, the distances are very similar to those observed for the pure MPTBs. The refinements do provide clear information on the metal sites with rhodium/tungsten mixed
occupancy. In addition, the refinements for both (Rh,W)-MPTB of the two crystal structures are given in Figure 4. Both show are given in the Experimental Section. Graphical representations Table 4. (Rh\textsubscript{19}W\textsubscript{65}O\textsubscript{136}(PO\textsubscript{4}\textsubscript{3})\textsubscript{24}. Atomic coordinates and isotropic displacement parameters.

| Atom | x   | y   | z   | s. a. f. | U\textsubscript{eq} [Å\textsuperscript{2}] |
|------|-----|-----|-----|---------|------------------|
| W1   | 0.0252(2) | 0.4104(6) | 0.04236(2) | 0.0708(6) | 0.0142(2) |
| Rh1  | 0.0252(2) | 0.4104(6) | 0.04236(2) | 0.2926(2) | 0.0142(2) |
| W2   | 0.25049(15) | 0.24727(5) | 0.37161(2) | 0.00929(12) |
| P    | 0.2478(2) | 0.0604(3) | 0.18620(11) | 0.0079(4) |
| O1   | 0.9632(2) | 0.2898(14) | 0.0006(6) | 0.0182(2) |
| O2   | 0.213(3) | 0.2505(13) | 0.1383(5) | 0.0262(5) |
| O3   | 0.2282(2) | 0.1205(10) | 0.2701(4) | 0.0162(4) |
| O4   | 0.033(1) | 0.0487(15) | 0.4064(5) | 0.0172(4) |
| O5   | 0.5322(2) | 0.1205(2) | 0.4044(5) | 0.0182(2) |
| O6   | 0.5492(2) | 0.3992(3) | 0.3188(6) | 0.0252(2) |
| O7   | 0.022(2) | 0.4772(3) | 0.3288(6) | 0.022(2) |
| O8   | 0.281(2) | 0.4901(12) | 0.4599(4) | 0.021(2) |

The original papers on the pure tungsten MPTBs). In contrast, [MO\textsubscript{4}] with only one or no adjacent phosphate group are partly occupied by rhodium. For the m = 7 phase even a systematic increase of Rh\textsuperscript{3+} occupancy with increasing distance from the phosphate tetrahedra (from the interface between the ReO\textsubscript{4}-like slabs) is observed. This cation ordering is rather surprising since valence sum considerations would suggest just the opposite ordering scheme for Rh\textsuperscript{3+}/W\textsuperscript{6+}, as is shown by the following considerations along the lines of Paulings rules and Browns equal valence rule.\cite{27} In the crystal structures of the mono-phosphate tungsten bronzes all oxygen atoms are twofold coordinated (P + W, P + Rh, W + W, W + Rh, Rh + Rh). Assuming ideal valence distribution within the coordination polyhedra [PO\textsubscript{4}](W\textsubscript{8} = 3/4), [WO\textsubscript{4}](W\textsubscript{8} = 2/3), and [RhO\textsubscript{4}](Rh\textsubscript{8} = 3/6) leads to "overbonded" oxygen when coordinated by P + W (\textSigma\textsubscript{V} = 9/4). For W + W (\textSigma\textsubscript{V} = 12/6), P + Rh (\textSigma\textsubscript{V} = 13/4, W + W (\textSigma\textsubscript{V} = 9/6), W + Rh (\textSigma\textsubscript{V} = 15/6) the valence sum for oxygen drops from ideal to strongly "underbonded". Allowing slight alteration of interatomic distances would result in some relaxation.\cite{28} However, exchanging tungsten by rhodium in [MO\textsubscript{4}] octahedra linked to phosphate would already avoid all unfavorable valence sums for oxygen, i.e. those in contrast to Paulings rule of preservation of local electroneutrality.\cite{27} Yet, this is not observed. One explanation might lay in an additional contribution to lattice energy from charge density modulation along the crystallographic c-axis in these structures. In other words, slabs with over bonded and under bonded oxygen (surplus of positive and negative charges, respectively) would stack along the crystallographic c-axis.

All crystals of (Rh\textsubscript{19}W\textsubscript{65}O\textsubscript{136}(PO\textsubscript{4}\textsubscript{3})\textsubscript{24} (m = 6) selected for SXRD structure analysis showed diffuse streaks in sections of the reciprocal space (see Figure S10). No reasonable integration of the reflections was possible. We relate this problem to the presence of severe stacking faults and variable thickness of the ReO\textsubscript{4}-like slabs.

Table 3. Summary on data collection and refinement of the crystal structures of (Rh\textsubscript{19}W\textsubscript{65}O\textsubscript{136}(PO\textsubscript{4}\textsubscript{3})\textsubscript{24} and (Rh\textsubscript{19}W\textsubscript{65}O\textsubscript{136}(PO\textsubscript{4}\textsubscript{3})\textsubscript{24}.
Electron microscopic investigation

SAED pattern and HRTEM images taken from crushed crystals of (Rh$_{0.05}$W$_{0.95}$O$_{14}$)PO$_4$ and (Rh$_{0.07}$W$_{0.93}$O$_{14}$)PO$_4$ are displayed in Figure 5. The lattice parameters derived from both SAED patterns accord well with the values obtained from XRD. No hints were found for the presence of superstructures.

The HRTEM images are in agreement with the structure models deduced from SXRD refinement, as it can be seen from overlaying a structural image based on coordination polyhedra (Figure 5). The characteristic fish-bone pattern with rows of ReO$_2$-like slabs and phosphate groups in between are nicely matched. A prominent characteristic of these MPTB structures are the pentagonal tunnels, which are formed between the ReO$_2$-slabs and phosphate groups and display a better white-contrast every second time along [001]. In previous electron-microscopic studies this effect was also observed and investigated. The contrast in MPTB’s is very sensitive to crystal tilting near [100] and the crystal thickness. The varying contrast therefore can be explained with a slight misalignment to the zone axis [100] and an unfavorable crystal size.

Images taken with lower magnifications show highly ordered ReO$_2$-like slabs with equal thickness, therefore, providing no hints on stacking faults. This result disagrees with the observation, that the intensities of the reflections (0 0 2) and (0 4) are different from the observed intensities of the XRPD data. It is also in contrast to the observation of significant diffuse scattering observed by SXRD for all (Rh,W)-MPTB. Several explanations are possible: Stacking faults occur in some crystals only and are not seen in the areas investigated by HRTEM or the ratio of rhodium/tungsten differs between ReO$_2$-like slabs within a crystal.

Electronic spectra and magnetic behavior of the (Rh,W)-MPTB

Powders of the (Rh,W)-MPTBs ($m=4$ and 7) are dark green in contrast to the orange-yellow of Rh(PO$_4$)$_3$ (C-type; [RhPO$_4$]$^2_-$ chromophore), which we discuss here as reference material. The color difference is in line with powder reflectance measurements of the three compounds shown in Figure 6. For Rh(PO$_4$)$_3$ the two strong absorption bands at 21500 cm$^{-1}$ and 28000 cm$^{-1}$ can be assigned to the ligand field transitions $^{1}A_{1g}→^{2}T_{1g}$ and $^{3}A_{1g}→^{2}T_{2g}$ of the octahedral [Rh(PO$_4$)$_3$] chromophore. Graphical evaluation according to Tanabe and Sugano [30] results in $B=430$ cm$^{-1}$ and $\Delta=23200$ cm$^{-1}$. These values are in good agreement with those determined for the [RhF$_6$]$^+$ chromophore in K$_2$RhF$_6$ ($B=460$ cm$^{-1}$, $\Delta=22300$ cm$^{-1}$). In contrast to Rh(PO$_4$)$_3$ and K$_2$RhF$_6$ the (Rh,W)-MPTBs show a broad absorption band in the NIR/vis ranging from 5000 cm$^{-1}$ to 14000 cm$^{-1}$ and a second in the vis/UV ranging from 19000 cm$^{-1}$ to 29000 cm$^{-1}$ (see Figure 6). The minimum around 17000 cm$^{-1}$ readily explains their green color. The absorption in the NIR/vis is reminiscent to those observed for blue heteropolytungstates, e.g. WO$_3$F$_{19/21}$ [31] or for electrochromic tungsten bronzes, e.g. Na$_2$WO$_3$ [32] and might thus point to the presence of some W$^{4+}$ besides W$^{6+}$ and Rh$^{3+}$. The ligand-field transitions for the [Rh(PO$_4$)$_3$] chromophore are not resolved in the (Rh,W)-MPTBs, most likely they are superimposed by LMCT ($\sigma^*-\pi^*$).

Angular overlap modelling (AOM) [33] has been used to reproduce the d-electron energy levels of Rh$^{3+}$ in Rh(PO$_4$)$_3$. For the AOM calculations the PC program CAMMAG [34] in a modified version [35] was used. Best fit AOM parameters obtained from the optical spectrum of Rh(PO$_4$)$_3$ are $B=490$ cm$^{-1}$ ($\beta=0.80$), $C=1960$ cm$^{-1}$, $\zeta=1408$ cm$^{-1}$, $e_s$(Rh$-$O) $\rightarrow$ d(Rh$-$O) -5.0 and $e_s$(Rh$-$O)$_{max}=11300$ cm$^{-1}$. Isotropic $\pi$-interaction Rh$-$O was assumed to be 1/4 of the corresponding $\sigma$-interaction $\langle e_s$(Rh$-$O)$\rangle=1/4 e_s$(Rh$-$O). As can be seen from the comparison in Figure 6, results from AOM match well with the observed energies for the transitions $^{1}A_{1g}→^{2}T_{1g}$, $^{3}A_{1g}→^{2}T_{2g}$, $^{3}A_{1g}→^{2}T_{3g}$ and $^{1}A_{1g}→^{2}T_{3g}$ of the [Rh(PO$_4$)$_3$] chromophore.

For Rh$^8$(PO$_4$)$_3$ and the (Rh,W)-MPTBs with the ideal compositions (Rh$_{0.85}$W$_{0.15}$O$_{14}$)PO$_4$ and (Rh$_{0.85}$W$_{0.15}$O$_{14}$)PO$_4$ one could expect diamagnetic behavior due to the $d^8$ configuration of W$^{6+}$ and the $^{3}A_{1g}$ electronic ground state of Rh$^{3+}$ ($d^6$, low-spin). However, considering a second-order Zeeman effect for...
Rh$^{3+}$ would lead to a small magnetic moment independent of temperature (TIP) according to van Vleck’s equation. Indeed, this expectation is perfectly met by the temperature independent susceptibility observed for Rh(PO$_3$)$_3$, $\chi_{\text{TIP}} = +100 \cdot 10^{-6}$ emu·mol$^{-1}$ (Figure 7). This value is also in agreement with measurements for Rh$^{3+}$ (e.g. RhCl$_3$, $\chi_{\text{TIP}} = +85 \cdot 10^{-6}$ emu·mol$^{-1}$; Rh$_2$(SO$_4$)$_3$·12 H$_2$O, $\chi_{\text{TIP}} = +95 \cdot 10^{-6}$ emu·mol$^{-1}$; $\text{[Rh}_3\text{O(CH}_3\text{COO})_6\text{]}_3\text{ClO}_4$, $\chi_{\text{TIP}} = +280 \cdot 10^{-6}$ emu·mol$^{-1}$; all $\chi$ per formula unit). Furthermore, the results from angular overlap modelling that already matched the excited state energies for the [Rh$^{\text{III}}$O$_6$] chromophore are fully consistent with the observed TIP for rhodium(III) metaphosphate (Figure 7). In contrast, the (Rh,W)-MPTBs show much higher molar susceptibilities ($\chi_{\text{TIP}}(\text{Rh}_{1.164}\text{W}_{6.836}\text{P}_4\text{O}_{32}) = +299 \cdot 10^{-6}$ emu·mol$^{-1}$), $\chi_{\text{TIP}}(\text{Rh}_{1.04}\text{W}_{12.96}\text{P}_4\text{O}_{32}) = +470 \cdot 10^{-6}$ emu·mol$^{-1}$; both obtained from a linear fit to the respective graphs of $\chi_{\text{mol}}$ vs. $T$ shown in Figure S11, plot of $\mu_{\text{eff}}$ vs. $T$ see Figure S12) which cannot be rationalized on basis of the exclusive presence of [Rh$^{\text{III}}$O$_6$] (Figure 7).

Figure 5. Top: Selected area electron diffraction (SAED) pattern of (Rh$_{1.666}$W$_{5.333}$O$_{32}$(PO$_2$)$_4$)$_4$ (a) and (Rh$_{2.041}$W$_{18.959}$O$_{32}$(PO$_2$)$_4$)$_4$ (c) in [1 0 0] zone axis orientation. Bottom: Fourier-filtered HRTEM image (CM30 T) of (Rh$_{1.666}$W$_{5.333}$O$_{32}$(PO$_2$)$_4$)$_4$ (b) and (Rh$_{2.041}$W$_{18.959}$O$_{32}$(PO$_2$)$_4$)$_4$ (d) in [1 0 0] zone axis orientation with overlaid structure of the MPTBs.
Subtracting $\chi_{\text{m}}(\text{Rh}^{3+}) = +100 \cdot 10^{-6}$ emu $\cdot$ mol $^{-1}$ from $\chi_{\text{mol,exp}}$ of the (Rh,W)-MPTBs still leaves for both significant contributions to the overall magnetic susceptibility. Two explanations, both related to the presence of W$^{5+}$ (d$^{1}$ electronic system, $^{4}T_{2g}$ electronic ground state for the octahedral chromophore [W$^{5+}$ $O_{6}$]), appear to be possible. Neither would lead to simple Curie-Weiss behavior. Magnetic behavior of sodium tungsten bronzes Na$_{x}$W$_{1-x}$O$_{3}$ might serve as comparison.\cite{44} Therein reported susceptibilities, due to the Pauli paramagnetism\cite{33,34} of delocalized electrons, are far too small to provide a reasonable explanation for the TIP of the (Rh,W)-MPTBs. A second approach for understanding might be based on the paramagnetism of localized electrons in W$^{5+}$. Yet, due to strong spin-orbit coupling and the wide variability of ligand field effects in 5d ions predictions on the paramagnetic behavior of W$^{5+}$ containing compounds are hard to make. Comparison to simple, magnetically well characterized systems (e.g. CsW$^{5+}$F$_{6}$, CsW$^{5+}$Cl$_{6}$)\cite{33,34} suggests a rather high content of up to 50 % W$^{5+}$ of the total tungsten content of the (Rh,W)-MPTBs. This seems to be unrealistically high by any means. Given the overall rather small susceptibilities of the (Rh,W)-MPTBs leaves eventually just the assumption of contributions of unidentified paramagnetic impurities as explanation. In this context it is worth noting that magnetic susceptibility data obtained for two batches of the (Rh,W)-MPTB at $m = 4$ (powder synthesis and crushed crystals from CVT) were almost identical. Clearly, characterization of the electronic structure of the (Rh,W)-MPTBs requires additional work, which is ongoing.

Seemingly, different experimental data (synthesis, SXRD, optical spectroscopy, magnetic measurements) for the (Rh,W)-MPTBs suggest different chemical composition for these phases. Thus, a critical review of these data with respect to the chemical composition of the phases under investigation is justified.

Syntheses based on the ideal compositions (exclusively Rh$^{3+}$ and W$^{6+}$) (Rh$_{21/2}$W$_{19/2}$O$_{32}$ (phase at $m = 4$) and (Rh$_{21/2}$W$_{19/2}$O$_{32}$ (phase at $m = 7$) led to single phase powder samples according to XRPD analysis of the solid reaction products. By-phases as consequence of deviations in composition will only be observable for an estimated amount higher than 3 %wt.

Structure refinements from SXRD data suggest small deviations from the ideal Rh/W ratio with slightly higher tungsten content than expected. Even though there is some correlation between site occupancy factors for Rh/W and the corresponding displacement parameters, we believe that the rhodium content of the two (Rh,W)-MPTBs is indeed slightly lower than expected for the ideal composition. Yet, the composition from SXRD might be regarded as the lower limit of rhodium content. While no hints on stacking faults in the (Rh,W)-MPTBs were obtained from HRTEM and SAED, diffuse scattering observed in SXRD patterns point to such defects which possibly will lead to deviations in stoichiometry.

Color and powder reflectance spectra of the (Rh,W)-MPTBs are strikingly different than what is observed for the perfectly stoichiometric and electronically well-defined metaphosphate Rh$^{3+}$(PO$_{4}$)$_{3}$. Strong bands in the NIR/vis region suggest mixed-valency W$^{5+}$/W$^{6+}$, yet already less than 1 % of W$^{5+}$ would be sufficient to cause such an absorption behavior, as is evidenced by the deep blue color of under-stoichiometric WO$_{3}$-\cite{33,34}

Magnetic susceptibility data of (Rh$_{21/2}$W$_{19/2}$O$_{32}$ (PO$_{4}$)$_{4}$ and (Rh$_{21/2}$W$_{19/2}$O$_{32}$ (PO$_{4}$)$_{4}$ do show, as expected, weak paramagnetism.
Yet, the absolute numbers cannot be rationalized solely based on the TIP expected for Rh$^{3+}$.

Results from EDS analyses (see Table 6) of crystals from CVT seem also to indicate a slightly smaller ratio Rh/W than related to the ideal compositions of the (Rh,W)-MPTBs. Yet, these analyses (including a ZAF correction) overestimate the light elements (phosphorus content) and underestimate heavy elements (Rh, W).

Summarizing these critical considerations, we believe that the obtained (Rh,W)-MPTBs do indeed show a slightly lower ratio Rh/W than that of the “ideal” compositions. Clearly, these phases do contain a small but significant amount of W$^{6+}$. Structural investigations did not give any hint on variations of the metal/phosphorus ratio in the (Rh,W)-MPTBs.

Conclusions

In extension of previous work it is shown that in MPTBs (WO$_3$)$_5$(PO$_4$)$_3$, substitution of W$^{6+}$ by appropriate combinations of Rh$^{3+}$ (or Ir$^{3+}$) and W$^{5+}$ is possible. Thus, new mm-MPTBs with the ideal compositions (Rh$^{3+}_{1/2}$W$_{5/6}$O$_{19/21}$)(PO$_4$)$_3$ (Rh$^{3+}_{1/2}$W$_{5/6}$O$_{19/21}$)(PO$_4$)$_3$ and $\text{Ir}^{3+}_{1/2}$W$_{5/6}$O$_{19/21}$)(PO$_4$)$_3$ are compared to simulations which are based on the data from single crystal structure analysis or isotypic compounds with matched lattice parameters and a suitable chemical composition (Figure 1). Tables containing the assigned reflections from the Guinier photograph are available online as Supplementary Material (Table S1–4).

Experimental Section

X-ray powder diffraction. Powder diffraction pattern for phase identification and purity control were recorded at ambient temperature using an imaging plate (IP) Guinier camera (HUBER G670, Cu-K$_\alpha$, radiation, $\lambda = 1.54059$ Å, 15 minutes exposure time in the angular range $4^\circ \leq 2\theta \leq 100^\circ$). The observed powder diffraction pattern of (Rh$_{1/2}$W$_{5/6}$O$_{19/21}$)(PO$_4$)$_3$, (Rh$_{1/2}$W$_{5/6}$O$_{19/21}$)(PO$_4$)$_3$ and (Rh$_{1/2}$W$_{5/6}$O$_{19/21}$)(PO$_4$)$_3$ are compared to simulations which are based on the data from single crystal structure analysis or isotypic compounds with matched lattice parameters and a suitable chemical composition (Figure 1).

Single-crystal X-ray diffraction. Suitable crystals of (Rh$_{1/2}$W$_{5/6}$O$_{19/21}$)(PO$_4$)$_3$ and (Rh$_{1/2}$W$_{5/6}$O$_{19/21}$)(PO$_4$)$_3$ were selected carefully under a polarizing microscope and glued to glass fibers. Diffraction data (graphite-monochromated Mo-K$_\alpha$ radiation; $\lambda = 0.71073$ Å) were collected using a Bruker Nonius $\kappa$-CCD area-detector diffractometer (BRUKER AXS B.V., Delft, Netherlands) which was controlled by the Nonius “Collect” software. For data processing the software package “HKL2000: Denzo & Scalepack” was employed.

A semi-empirical absorption correction based on multiscans was applied to the diffraction data using the program package Platon.

Table 6. Ideal and analytical composition of "(Rh$_{1/4}$W$_{5/6}$O$_{19/21}$)(PO$_4$)$_3$" (m = 4) and "(Rh$_{2/7}$W$_{19/21}$O$_{33/31}$)(PO$_4$)$_3$" (m = 7).

|        | Rh [\%] | W [\%] | P [\%] |        | Rh [\%] | W [\%] | P [\%] |
|--------|----------|--------|--------|--------|----------|--------|--------|
| ideal composition | 11.11 | 55.56 | 33.33 | 7.41 | 70.37 | 22.22 |
| SXRD | 9.71 | 57.01 | 33.33 | 5.85 | 72.15 | 22.22 |
| EDS (REM)[$^a$] | 11.0(8) | 50(2) | 39(3) | 7.1(6) | 67(3) | 26(2) |

[$^a$] Area measurement of single crystals.
were measured during cooling and heating. At each temperature step a series of ten measurements were taken. Only close to ambient temperature, slight differences between the data obtained on cooling or heating were observed. The susceptibility data shown in Figure 7 have been corrected for capsule and diamagnetic contributions. Furthermore, a low content of ferromagnetic impurity was corrected with a Honda-Owen plot. Therefore, measurements with a different external field (0 to 20000 Oe) were conducted at 150 and 300 K for all samples. All susceptibilities are given for 1 mole (formula unit) of the compound. In case of the MPTBs the sum formula according to SXRD was used.

Deposition Numbers 2062902 (for Rh$_{20}$W$_{25}$O$_{75}$ (PO$_4$)$_3$ (phase at $m=4$)), and 2062903 (for Rh$_{20}$W$_{25}$O$_{75}$ (PO$_4$)$_3$ (phase at $m=7$)) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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The authors declare no conflict of interest.

Keywords: Equilibrium relations · MPTB · Rhodium · Iridium · Solid-state chemistry · Solid-state structure

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