Multiple Bonds between Main-Group Elements and Transition Metals. 137.1 Polymeric Methyltrioxorhenium: An Organometallic Nanoscale Double-Layer Structure of Corner-Sharing ReO₅(CH₃) Octahedra with Intercalated Water Molecules†


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Abstract: A two-dimensional structural model of polymeric methyltrioxorhenium (MTO) has been established by means of diffraction techniques and a variety of analytical methods. The unusual compound, constituting the first example of a polymeric organometallic oxide, has a layer structure of methyl-deficient, corner-sharing ReO₅(CH₃) octahedra. It adopts the three-dimensional extended ReO₅ motif in two dimensions as a \{ReO₅(CH₃)\}_n network. Adjacent layers of corner-sharing ReO₅(CH₃) octahedra (A) are capable of forming staggered double layers (AA'). In the crystalline areas of "poly-MTO", such double layers are separated by intercalated water molecules (monolayer) (B) with an ...AA'BAA'... layer sequence. For the partially amorphous areas of "poly-MTO", we propose a turbostratic and 00l-defect stacking model for the "poly-MTO" and water layers. Interactions between the adjacent layers in this polymeric MTO are very weak, resulting in graphite-like macroscopic properties such as flaky appearance, softness, and lubricity. High electric conductivity results from understoichiometry with respect to the CH₃Re ratio (9.2/10) and partial reduction by extra hydrogen equivalents. For the purpose of comparison, the solid-state structure of "monomeric" MTO as established by a combination of X-ray and powder neutron diffraction techniques is also reported.

Introduction

The synthesis and properties of the novel organometallic polymer 1 of empirical formula \{H₀.₅(CH₃₀.₉₂ReO₃)}_x were described in the preceding paper.1 Here we establish a structural model of this remarkable compound. Transmission electron and X-ray diffraction are the main techniques used to study the unique structure of this organometallic polymer.

Chemical and Physical Data for a Consistent Structure Model

The title compound, for simplicity called "poly-MTO", forms from dilute aqueous solutions of methyltrioxorhenium(VII) (MTO) as a highly dispersed golden-colored precipitate. The empirical formula \{H₀.₅(CH₃₀.₉₂ReO₃)}_x (1) is close to that of the monomeric precursor CH₃ReO₃. The observed odd stoichiometry results from an inherent methyl deficiency (approximately 8%) and from additional hydrogen content (approximately 1 mol of H per 2 mol of Re). These extra hydrogen atoms result from reduction of MTO during formation of 1 (eq 1).4 The presence of acidic hydrogen is typical of "classical" bronze-type structures such as H₂ReO₄ with x < 0.2 (empirical eqs 1 and 2).

\[
\text{CH}_3\text{ReO}_3 + \text{H}_2\text{O} \rightarrow \nonumber
\]

\[
\{\text{H}_0.5(\text{CH}_3)0.92\text{ReO}_3\}_x + \text{O}_2 + (\text{HReO}_4 + \text{CH}_4) \quad (1)
\]

1: ca. 70% yield ca. 30% yield

\[
\text{ReO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{ReO}_3 + \text{HReO}_4 \quad (x < 0.2) \quad (2)
\]

The electric resistivity of 1 amounts to \(6 \times 10^{-3} \, \Omega \cdot \text{cm} \) at 25 °C, resembling that of violet ReO₃ (10⁻² Ω·cm). Since crystalline, pure ReO₃ is formed thermally from both 1 and H₂ReO₄, structural interrelations are reasonable to assume (Figure 1). The density of 1 (\( \rho = 4.38 \, \text{g} \cdot \text{cm}^{-3} \)) at 23 °C, measured pycnometri-

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Figure 1. Typical transformations of “polymeric” methyltrioxorhenium (I). *Moist atmosphere, solid-state reaction.

Figure 2. Molecular structure of monomeric CDiReO3 at 5 K based on a powder neutron diffraction study (PLATON\textsuperscript{(b)} drawing showing the 90% probability ellipsoids). Important distances and angles of the solid-state structure are given in comparison (in brackets) with the gas-phase electron diffraction data. Re-O: 170.9(3); C-Re-O: 113.0(3); C-D1: 108.2(3); C-D2: 109.6(2); C-H: 105.4(5). All distances are in pm and angles in deg.

Figure 3. SCHAKAL\textsuperscript{(a)} drawings of the MTO structure (neutron diffraction). (top) Closed-packed CH3ReO3 tetrahedra in the solid state. (bottom) MTO molecules located in the middle of a coordination polyhedron formed by 14 neighboring molecules.
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The layer structure evident from diffraction studies is based on a [ReO2]_n- network (Figure 6). How does this model fit the analytically determined net formula \{H_0.5[(CH_3)0.92ReO_3]\}_n? From simple stoichiometric considerations, one should expect approximately one methyl group, one oxo group, and about one-half extra hydrogen equivalent per rhenium atom in addition to ReO_3. Quantitative 1H NMR experiments indicate that every methyl group present (CH_3/Re = 0.92/1.0) is bound to rhenium. In addition, complete formation of CH_3Re(O_2)OH_2\textsuperscript{2+} from

of all reflections of every second row.

Table 1. Crystallographic Data of "poly-MTO" and ReO$_3$

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"poly-MTO"—based on the fraction of methyl groups—has been observed.1 Finally, the unusual "depolymerization" $I \rightarrow$ MTO (plus some ReO$_3$) suggests that the methyl and oxo groups are in a chemical environment similar to that in solid MTO. Monomeric units of MTO were detected when $I$ was subjected to the conditions of FT-ICR and FAB mass spectrometry.1

While proton NMR spectroscopy of paramagnetic molecular solids is already well established, the first examination of an organomeric polymer by paramagnetic NMR spectroscopy is presented here. Single-pulse excitation solid-state $^1H$ wide-line NMR measurement of amorphous $I$ in a solenoid probehead yielded the spectrum shown in Figure 7a. Two distinct signals are visible. Both the small line width (ca. 2.2 kHz) and the Lorentzian signal shape of the high-field resonance are indicative of protons attached to a highly mobile group. We therefore assign this signal tentatively to the protons of the methyl group which rotates about its 3-fold axis. This assignment is further supported by the chemical shift within the diamagnetic range (0 ppm). The second broad signal (half-width ca. 25 kHz) must correspond to protons near paramagnetic centers because of the chemical shift at $\delta = 80$ ppm. The presence of traces of water in the sample cannot be excluded, since both signals are obviously sitting on a broad hump which spans the spectral range from $-150$ to $+150$ ppm (the presence and functionality of water will be discussed later). The $^1H$ wide-line NMR spectrum of a polycrystalline sample of diamagnetic MTO shows a textbook example of dipolar coupling of three spin-$^{1/2}$ nuclei in close proximity (Figure 7b).1

Acidic protons have been located by neutron diffraction techniques in related compounds such as $H_{0.53}WO_3$ and $H_{36}-ReO_3$.12 One may postulate that hydrogen in $I$ is similarly attached to oxygen atoms of Re-O-Re bridges. In typical "bronze-type" structures, edge-bridging oxygens are (partially)protonated and $O-H$ bond distances of approximately 10 pm are observed.12 Terminal oxo groups seem to exhibit less Lewis basicity. For example, the related compound ($\text{Si}_5-C_5$-Me$_2$)$_2$ReO$_3$ is protonated only at the oxo bridges and forms also hydrogen bridges at these positions with water,13 $CH_2ReO_3$ is not protonated even with very strong Brønsted acids.14 An earlier model15 which proposed the layers interconnected by
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hydrogen (proton) bridges of type Re=O⋅H⁺⋅O=Re is not supported by a theoretical treatment of the problem. The molecular orbital calculations indicate that the observed electric conductivity arises from protonation within the ReO₃ layer.

Since partial demethylation generates a certain concentration of paramagnetic Re⁶⁺ centers, ESR spectroscopy was also applied. The low-temperature ESR spectra of I and ReO₃ are strikingly similar (322 mT, 9.06 GHz for I; 323 mT, 9.05 GHz for ReO₃). ReO₃ shows one signal without a resolved hyperfine splitting (I = 7/2, Re and Re⁶⁺). The ESR spectrum of the title compound I is complex and consists of at least three overlapping signals. Several paramagnetic centers as a result of statistical distribution seem to be present, just as suggested in our structure model. An ESCA study also supports the presence of Re⁶⁺ centers. The latter are responsible for the paramagnetic behavior of I at temperatures below 100 K. The temperature dependence of the molar magnetic susceptibility of I and ReO₃ is again very similar.

The {ReO₃} framework of Figure 6 gets completed by addition of an oxo and a methyl group, thus resulting in a layer-structure of corner-sharing ReO₃(CH₃) octahedra. This structural model adopts the three-dimensional extended ReO₃ motif in two dimensions as a {ReO₃} network (Figure 8).

The Re=C and Re=O bond distances should be slightly longer than those of (monomeric) MTO (Re=O, 1.702(2) Å; Re=C, 2.063(2) Å; Figure 2) since reduction by the extra hydrogen equivalents has occurred. The Re-⋯Re distance is identical with the cell constant a = 3.728(1) Å. There is no evidence as to the geometry of these Re−O−Re bridges, e.g. whether they are linear or not. In related systems, such as H₄MTO and H₁₃₀ReO₃, the M−O−M units (M = W, Re) are slightly bent (ca. 170°) as they get protonated to give M−(OH)−M moieties. In addition, there are no experimental data available to assign the "tacticity" (up or down) of the methyl vs oxo pattern in the structural model of I (Figure 8).

We propose a disordered model in which methyl-free rhenum(VI) sites are completely statistically distributed over the entire {ReO₃} network to explain the diffuse streaks along a* and b* in the electron diffraction pattern (Figure 5b). The sharp Bragg reflections result from positions of the rhenum atoms alone. These heavy atoms are the dominant scattering centers in the model. Their positions are obviously not much affected by the disorder problem. In one case, however, we could find another type of crystal showing sharp reflections.

Figure 6. Structural comparison of the three-dimensional cubic ReO₃ network (above) and the two-dimensional square {ReO₃} sheets (below).

Figure 7. 300 MHz wideline ¹H NMR spectra obtained by single-pulse excitation. (a) "Poly-MTO" (1) (3000 transients). The narrow signal at low frequency corresponds to methyl groups and the high-frequency broad signal to protons near paramagnetic centers. (b) Polycrystalline MTO (4000 transients); Resonance of methyl protons, for details see text.

Figure 8. Idealized two-dimensional model of the layer-structure of corner-sharing ReO₃(CH₃) octahedra. Four square unit cells are drawn. The positions of the acidic protons are not indicated since they are statistically distributed across the {ReO₃} planes. The positions of methyl-free rhenum (Re⁶⁺) are also statistically arranged. According to the analytical composition of I, ca. 8% of the original methyl groups are lost during formation of I from MTO in water. One demethylated rhenum site is indicated by a shaded circle in the first of the four unit cells.

References:
along (at least) one main direction of the reciprocal lattice (Figure 5c). The structure of this crystalline particle belongs to the orthorhombic system. The lattice constants calculated from this pattern are \( a = 3.81 \) and \( b = 11.16 \) Å \( (b = 3a \) within the accuracy of measurement). The ordering along the crystallographic axes in Figure 5c is obviously different from that in Figure 5a, causing the observed tripling of (at least) one lattice constant. This superstructure effect might be a consequence of the distortion of the ReO\(_5\)(CH\(_3\)) groups away from perfect octahedra as result of bent \( \text{M-O-M} \) units. As mentioned above, the \( \text{M-(OH)-M} \) units of \( \text{H}_0.5\text{WO}_3 \) and \( \text{H}_{1.3}\text{ReO}_3 \) are also slightly bent. In these cases the distortion of the MO\(_6\) octahedra resulted in a doubling of the lattice constants of the cubic cell.

The Three-Dimensional Model—A Double-Layer Structure with Intercalated Water

Up to now we solely concentrated on electron diffraction experiments on nearly completely dehydrated “poly-MTO” \( (1) \) under high-vacuum conditions. These samples result from extensive washing and drying procedures.\(^3\) In the X-ray powder diffraction experiments of \( 1 \), additional diffuse and broad reflections could be observed besides the \( hkl \) reflections (see above). These reflections gain intensity and narrow to smaller peak half-widths if moist samples of raw poly-MTO \( (1) \) from aqueous suspensions and without drying under high-vacuum conditions are recorded. Some of the additional peaks become the dominant peaks in the pattern (Figure 9) when measurements were carried out at small angles of incidence \( (2-6^\circ) \), thus being identified as the missing 00\( l \)-reflection series of “poly-MTO.”

The complete diffraction pattern could now be indexed on the basis of a tetragonal unit cell: \( a = 3.728(1) \); \( c = 16.516(5) \) Å (space group \( P4mm \)). Similar cell constants could also be found for inorganic bronze-type structures, e.g. \( \text{H}_3\text{MoO}_3 \),\(^{16a}\) which consists of two-dimensional double layers of face-sharing \( \text{MO}_3 \) octahedra. Assuming two layers of “poly-MTO” per unit cell leads to an average interlayer distance of 8.22 Å, which is compatible with one additional intercalated water layer.

The diffraction pattern of the water intercalation modification of \( 1 \) shows a weakening of all \( hkl \) reflections with \( h + k + l \) odd, implying a nearly body-centered unit cell with a staggered arrangement of the individual “poly-MTO” layers. Due to the centering the \( h00 \) reflections 100, 210, 300, and 320 (present in the electron diffraction pattern of \( 1 \)) are absent in the case of \( 1 \) while high intensities for the corresponding \( k0l \) reflections (101, 211, 301, and 321) are observed. By way of contrast the 00\( l \) reflections only show a weakening for the 001, 003, and 005 reflections. Obviously the body centering is nearly perfect regarding the \( a \) and \( b \) axes of the unit cell but not completely fulfilled along the \( c \) axis. This can be explained by a model in which the “poly-MTO” layer \( A' \) (being displaced by \( (a + b)/2 \) relative to \( A \)) should have two different interlayer distances toward both adjacent layers \( (A, A') \) with a resulting layer sequence of \( A-A'-A-A' \).

We propose that the two different interlayer distances of about 7.4 and 9.1 Å result from a layer arrangement in which the oxo groups of two adjacent layers are vis-à-vis (Figure 10), with a water layer \( (B) \) intercalated between the oxo groups of adjacent layers and a layer sequence of \( ABA'BA' \). This model allows the formation of hydrogen bridges between the water molecules and the oxo groups of adjacent “poly-MTO” double layers. The water molecules therefore play a dominant role in connecting such double layers. The observed loss of crystal-

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linity in vacuum-dried samples of 1 and the pronounced hygroscopicity of such samples thus finds a simple explanation in the important structural function of the intercalated water molecules. The unpolar methyl groups are oriented inside the double layer. The double layers are therefore interconnected by van der Waals attractions which are in agreement with the observed high lubricity of “poly-MTO”.

Interconnecting water layers of this kind are known for layer structures of clay minerals, e.g., montmorillonite. The unit cell of fully hydrated 1 comprises a close packing of the “poly-MTO” and water layers, so there is no space left for additional solvent molecules. (Only holes of about 8 Å in size are present, assuming water molecules centered at 002 (Figure 10) and resulting in a maximum amount of one water molecule per two “CH₃ReO₃” units.) However, the packing of corner-sharing CH₃ReO₃ octahedra in 1 seems energetically less favored as compared to the “isolated”, and close-packed tetrahedra of CH₃ReO₃ in the structure of MTO. It is thus no longer surprising that “poly-MTO” undergoes “depolymerization” under various conditions.

It was noted above that the intensities of the h00 reflections increase with increasing angle of incidence (Figure 9). This phenomenon indicates a preferred orientation of the crystalline flakes along the surface of the sample holder. The same is true for the recorded intensities of the 00l reflections: they increase with decreasing angle of incidence, in full agreement with such a preferred orientation (Figure 9).

Different peak half-widths for different classes of reflections are also observed: the h00 reflections are much narrower than the 00l and hkl reflections. This anisotropic broadening might arise from lattice distortion and disorder problems (e.g., defect broadening due to partial dehydration of 1) along the third crystal dimension or simply from a size effect due to nanoscale thickness of the layers. In addition, a polytypism effect due to alternative stacking arrangements of the water and “poly-MTO” layers could be responsible for the observed anisotropic broadening.

The calculated and observed X-ray diffraction patterns (ignoring the preferred orientation and the disorder problems) are shown in Figure 11. A neutron diffraction study is expected to improve and refine the structure of 1.

(a) Checking the Local Symmetry by Infrared and FT-Raman Spectroscopy.

The infrared spectra of of fully deuterated 1,9 of fully deuterated MTO10 have been discussed and compared in detail. To check the local symmetry of the suggested three-dimensional structure model, we recorded a FT-Raman spectrum of 1.

A factor group analysis was performed using Adams and Newton tables19 for the P4mm crystallographic space group. In case of Z = 2 molecules per primitive unit cell, the most characteristic Re=O and Re-C “axial”-stretching modes show 2A₁ and B₁ modes. The observed spectra are consistent with the results of factor group analysis: the B₁ modes are only Raman active while the A₁ modes are active in both the Raman and IR spectra (Figure 12). According to the above selection rules, three bands (2A₁ + B₁) were always observed in the Raman spectra, and there are only two bands in the infrared (2A₁) that coincide with the Raman frequencies. In case of MTO, only one Re=C stretching mode (A₁) is observed at 572 cm⁻¹ (IR and Raman spectra, respectively) in the solid state. As can be judged from the average position of the ν(Re=O) bands, the rhenium–oxygen bond strength is less than in MTO, for which the Re=O force constant is calculated at 8.15 Ncm⁻¹.18 A simplified calculation for “poly-MTO” gives 7.34 Ncm⁻¹. Slightly longer ReO bond distances in “poly-MTO” vs MTO (1.702 Å) are thus reasonable to assume and in agreement with our suggested model (Figure 10, Table 2).

The site symmetries of the rhenium position in 1 and ReO₃ are related by a group-subgroup relationship: O₉(ReO₃) → D₇₀ = C₇₀ (1). Due to the higher site symmetry in the case of ReO₃, only one IR-active Re=O stretching mode (Fₐ) is observed (913 cm⁻¹). In the case of MTO only one Re=C stretching mode (A₁) at 572 and 576 cm⁻¹ (IR and Raman spectra, respectively) can be recorded (site symmetry for the rhenium position is C₇₀).

(b) Further GED Investigations of Partially Amorphous Domains of 1. The electron diffraction experiments were performed on partially dehydrated “poly-MTO” (I) due to the high-vacuum conditions necessary for such experiments. The X-ray diffraction patterns of such samples show very broad 00l reflections. The same is true for the electron diffraction patterns of I—they do not yield a resolved three-dimensional reciprocal lattice: no hkl or 00l reflections were detected. Nevertheless the 00l reflections are still present because the electron diffraction pattern (Figure 5a) does not change very much upon tilting the goniometer except a little bit for the distances perpendicular to the tilt axis and the angles between the rows of reflections. The reciprocal space construction for such a two-dimensional diffraction consists of spread diffuse 00l rods parallel to e* (Figure 13). Such diffuse 00l rods correspond to the observed broad diffuse reflections in the X-ray diffraction pattern of 1 dried by standard procedures (high vacuum). A projection along e* results in the observed two-dimensional diffraction pattern of the reciprocal h00 plane (Figure 5a).

In one case, we also could observe the diffraction pattern shown in Figure 5e: this pattern results from extreme tilting of the crystalline flake along [110], and it is also in agreement with the proposed reciprocal space construction (Figure 13).

This effect is indicative for a strongly disordered stacking of such layers (either parallel to a, b, or c) and is supported by a size effect due to nanoscale thickness of the layers. So far none of the crystals (about 2 μm in diameter) could be imaged under high-resolution conditions because they rapidly deteriorated on increasing the intensity of the electron beam. Obviously the thickness of these crystalline flakes escapes our determination. However, we assume a nanoscale thickness of only a few unit
cells due to the high transparency of the observed crystalline flakes. Suspensions of the substance in water thus favor separation and preferred orientation of the "poly-MTO" layers on the support grid, resulting in the usually observed diffraction pattern of Figure 5a. The same preferred orientation phenomenon has been observed in the X-ray diffraction experiments (see above). SEM and a TEM images of sedimented "poly-MTO" flakes nearly aligned along the surface of the sample holder are shown in Figure 14, parts a and b, respectively.

Diffraction patterns of such overlapping "twisted layers" as shown in Figure 5d are to be interpreted as powder patterns that still show only resolved hkl reflections. In no case were resolved 00l reflections observed. This demonstrates again that the presence of water plays an important role for the three-dimensional order in "poly-MTO". Nevertheless indications of a third dimension are seen in one case (Figure 5f): every second row of reflections is weakened here, with the layers obviously not being twisted but rather systematically translated along one crystallographic main direction (approximately half the lattice constant).

(c) Model for the Amorphous Domains of 1. Up to now all diffraction experiments were dealing with the crystalline (hydrated) or partially crystalline (partially dehydrated) domains of 1. This investigation shows that the crystallinity and the ordering of the "poly-MTO" layers is strongly influenced by the amount of water. However, it cannot be concluded from these results that the amorphous bulk domains of 1 do not exhibit any kind of interlayer ordering. If one considers a simple three-dimensional model of eclipsed layers of corner-sharing ReO$_5$-(CH$_3$)$_6$ octahedra (TlAlF$_4$-type), an average interlayer distance of about 6.8 Å is calculated from the observed density ($\rho = 4.38$ g cm$^{-3}$). This distance is consistent with theoretical calculations, according to which interlayer distances smaller than 6 Å imply a significant destabilization due to van der Waals repulsions between individual layers. Such an eclipsed model is compatible with the tetragonal unit cell (see above). An alternative, staggered packing of adjacent layers is represented by a SnF$_2$/SnF$_3$[SnF$_4$]$_2$-type model.

We explain the lack of pronounced ordering along the third dimension in the amorphous domains by the complete lack of intercalated water molecules and therefore by small interlayer interactions and variable interlayer distances originating from more or less statistically alternating ("atactic") methyl and oxo group positions.

(d) Quantification of the Water Content in 1 by TGA-MS Investigations. It is important to stress that the empirical formula $\{\text{Ho}_{0.5}[(\text{CH}_3)_{0.92}\text{ReO}_3]\}_{\infty}$ accounts for samples prepared under standard conditions (washing with water, ether, THF, and pentane and drying under high-vacuum conditions). Nevertheless, careful inspections of the TGA-MS measurements reveal that also in these samples traces of water are still present. This is in agreement with the observed X-ray diffraction pattern which shows also for such vacuum-dried samples 00l reflections indicative of the water layer. Also the IR spectra and the solid-state $^1$H NMR spectra (discussed above) are in agreement with the assumption that traces of water are inherently present in 1. The presence of water has been taken into consideration in the new formula for 1: $\{\text{H}_{0.5-2x}[(\text{CH}_3)_{0.92}\text{ReO}_3]_{\infty}\}$.

Quantification of "x" by TGA-MS Investigations. Samples of 1 (freshly synthesized in D$_2$O and "dried" under high-vacuum conditions (turbo-pump coupled with MS, 10$^{-5}$ Torr) show even after 3 days a significant D$_2$O signal (m/z = 20). To quantify the amount of intercalated water, we performed TGA-
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Figure 12. Re=O and Re=−C stretching modes in “poly-MTO”, see text.

Quantification by Stoichiometry. The amount of “extra hydrogen atoms” in \( \{H_{0.3}[(CH_3)_{0.7}ReO_1]\}_x \) provides the upper limit of the water content: \( x_{\text{max}} = 0.25 \). This upper limit is in agreement with the experimental value in the range of the systematic limitations of both methods: elemental analysis and TGA-MS. The water and the acidic protons are detectable simultaneously by the solid-state NMR experiment, so \( x < 0.25 \) should be smaller than this stoichiometric limit: \( x < 0.25 \).

Crystallographic Considerations. Assuming the water molecules are located at 00z, only “holes” of about 8 Å in size are present in the unit cell. Therefore no space is left for additional water molecules and therefore an ideal value of \( x_{\text{ideal}} = 0.5 \) should be the upper limit for completely hydrated samples of 1. At this stage it is important to stress that not the crystalline but the amorphous domains constitute the dominant part of 1. Therefore, we still can assume a value of \( x = 0.5 \) for the crystalline portions of 1 and the value of \( x < 0.25 \) will still be valid for both domains (amorphous and crystalline).

For the partially amorphous areas we propose a model with turbostratic and 00l defect stacking of the double layers of corner-sharing ReO₆(CH₃) octahedra (see above). In these areas we expect a much lower value of \( x \) than in the crystalline areas resulting in an all over value of \( x < 0.25 \) (Figure 15).

It has to be stressed that the interlayer separation in 1 (Figure 10) does not vary as a function of \( x \). We showed that the intercalated water can hardly be removed by drying procedures under high-vacuum conditions. This accounts for the observation that there are always crystalline domains in 1 with intact water layers.

Figure 13. Reciprocal space construction. All reciprocal spots are spread out to form diffuse rods. Tilting of these thin layers leads to distortions of the square reciprocal lattice toward a “rhombic” reciprocal lattice.
The vacuum drying procedure simply reduces the portions of the hydrated, crystalline areas but does not affect the interlayer distance of the remaining hydrated areas. This is in agreement with the observation that only the 001 reflections are affected by the drying procedure (due to the loss of crystallinity) while the d-values remain invariant.

It has also to be emphasized that values of $x > 0$ cause a small understoichiometry with respect to the ReO ratio (1:3). We therefore cannot exclude that small amounts of amorphous ReO$_3$ are present in the bulk domains of I which account for this understoichiometry. (Re$^{IV}$ centers have been determined for I by ESCA, but they could be also generated by the experimental conditions.) Re$^{IV}$ centers inside the "poly-MTO" layers are unlikely and would suggest Re atoms lacking both the methyl and a terminal oxo group. Up to now Re$^{IV}$ centers in rhenium bronzes have only been observed for the high-pressure modification of ReO$_3$: the golden-colored Re$_{1.16}$O$_{3.623}$.

Conclusion

"Poly-MTO" is the first example of a polymeric organometallic oxide. The structure of the crystalline domains of I is best described by double layers of corner-sharing CH$_3$ReO$_5$ octahedra (AA°) with intercalated water molecules (B) (AA°/BAA°... layer sequence). The oxo groups of two adjacent layers are vis-à-vis (Figure 10), with a water layer (B) intercalated between the oxo groups of adjacent layers. This model allows the formation of H-bridges between the water molecules and the oxo groups of adjacent "poly-MTO" double layers. The water molecules therefore play a dominant role in connecting such double layers. The observed loss of crystallinity in vacuum-dried samples of I and the pronounced hygroscopicity of such samples thus find a simple explanation. The unpolar methyl groups are oriented inside the double layer.

The double layers are therefore interconnected by van der Waals attractions in agreement with the observed remarkable lubricity of "poly-MTO". High electric conductivity results from understoichiometry with respect to the CH$_3$/Re ratio (9.2/10) and partial reduction by extra hydrogen equivalents.

For the amorphous areas, we propose a model with turbostratic and 001 defect stacking of the double layers of corner-sharing ReO$_5$(CH$_3$) octahedra with smaller water contents.

As compared to the classical ReO$_3$-type structure, an additional CH$_3$ group present in I cannot act as a bridging ligand and connect adjacent layers. However, if this extra ligand eliminates under thermal or photochemical conditions, only small structural changes are necessary to transform the layer-type polymeric organometallic oxide I into the three-dimensional metal oxide ReO$_3$. This aspect of organometallic chemistry is new and warrants further exploration, e.g., in the formation of three-dimensional mixed perovskites by the introduction of ReO$_3$.

Experimental Section

Information concerning other analytical and chemical studies is summarized in the chemical part of this publication and in a thesis.

(1) X-ray Powder Diffraction. Powder diffraction patterns of I, ReO$_3$, Re$_3$, NH$_4$ReO$_4$, CH$_3$ReO$_5$, (CH$_3$)$_2$Re$_2$O$_6$, and (CH$_3$)$_3$ReO$_4$ were recorded using varying measuring conditions on three Guinier diffractometers supplied by HUBER with Ge or Si monochromators ($\lambda = 154.056$ pm) and computer-controlled single-channel NaI scintillation detectors. The data were collected with counting times and step widths in the range of $t = 2$–20 s and $\theta = 0.002$–0.01° (step-scanning method).

(a) "Poly-MTO". Samples of "poly-MTO" (I) were studied in both symmetric and asymmetric transmission geometries on a G642 Guinier diffractometer for flat powdered samples. Samples of I were ground in an agate mortar and stored on a foil (thickness < 0.02 mm) that was covered with a thin film of Vaseline. The diffraction patterns were found to be nearly independent of the grinding time. Obviously the dimensions of the crystalline nanoflakes are too small to be much influenced by common grinding procedures. Thin films of I (dried aqueous suspensions) were also studied on thin polypropylene foils.

Measurements at different angles of incidence ($\Psi = 2$–6°) were recorded on a Huber G642 Guinier diffractometer (symmetric transmission, angle of incidence $\alpha = 90°$; asymmetric transmission, $\alpha = 45°$), in back-reflection on a G653 Guinier thin-film diffractometer ($\alpha = 3$–6°), and also on a Siemens D5000 diffractometer ($\alpha = 2°$). Crystallographic data of "poly-MTO" (hydrated form) are as follows: tetragonal, $P4mm$ (Int. Tab. No. 99), $a = 3.728(1)$ Å, $c = 16.516(5)$ Å. In the X-ray diffraction pattern of raw "poly-MTO" samples, extra peaks belonging to the well-known dimeric compound (CH$_3$)$_2$Re$_2$O$_6$ (less than 4% by analysis) were detected by means of X-ray diffraction (powder and single-crystal methods). This compound exhibits two bridging oxo ligands. This "impurity" can be removed by washing samples of "poly-MTO" with water, diethyl ether, and THF. After this washing procedure, only the X-ray powder pattern of the title compound is present.

(b) ReO$_3$. Dry samples of "poly-MTO" (I) were ground in an agate mortar and sealed in thin quartz capillaries (0.5 mm i.d.; all operations performed in a glovebox). The capillaries were rotated continuously during heating and measuring (temperature range, 25–400 °C; $\Delta T$/scan, 25 °C; counting times, 20 s; step widths, $\theta = 0.02°$; measuring interval, $\theta = 8$–18°) on a G644 Guinier diffractometer equipped with a heating unit. The sample was tempered at 400 °C for 10 min of ReO$_3$ (measuring interval of $\theta = 2$–50°) was recorded at room temperature: orthorhombic space group Pnma (no. 60), $a = 4.806(2)$ Å, $b = 5.631(4)$ Å, $c = 4.623(2)$ Å.

(c) Re$_3$. Raw samples of "poly-MTO" (I) were ground in an agate mortar and sealed in thin quartz capillaries (0.3–0.5 mm i.d.). The capillaries were rotated continuously during heating and measuring (temperature range, 25–400 °C; $\Delta T$/scan, 25 °C; counting times, 10 s; step widths, $\theta = 0.01°$; measuring interval, 8–20°) on a G644 Guinier diffractometer equipped with a heating unit. The sample was tempered at 400 °C for 10 min of Re$_3$ (measuring interval of $\theta = 2$–50°) was recorded at room temperature: orthorhombic space group Pnma (no. 60), $a = 4.806(2)$ Å, $b = 5.631(4)$ Å, $c = 4.623(2)$ Å.

Figure 14. SEM micrograph (top, 11 000x magnification) and TEM micrograph (bottom, 25 000x magnification) of "sedimented flakes" of "poly-MTO" (I).
The flexible "intercalated" and absorbed water is partially removed by the standard drying procedure (vacuum).

Table 2. Coordinates of the Suggested and Idealized Structure Model of "Poly-MTO".\(^\text{a}\) \(\{\text{H}_2\text{O}\}_8\text{ReO}_3\) (observed stoichiometry)

<table>
<thead>
<tr>
<th>atom</th>
<th>(x/a)</th>
<th>(y/b)</th>
<th>(z/c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O1</td>
<td>(1/2)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O2</td>
<td>0</td>
<td>(1/2)</td>
<td>-1.060 40</td>
</tr>
<tr>
<td>C1</td>
<td>0</td>
<td>0</td>
<td>0.130 80</td>
</tr>
<tr>
<td>H1</td>
<td>0.171 50</td>
<td>0.171 50</td>
<td>0.151 40</td>
</tr>
<tr>
<td>H2</td>
<td>0.062 80</td>
<td>-0.234 20</td>
<td>0.151 40</td>
</tr>
<tr>
<td>H3</td>
<td>-0.234 20</td>
<td>0.062 80</td>
<td>0.151 40</td>
</tr>
<tr>
<td>Re2</td>
<td>(1/2)</td>
<td>(1/2)</td>
<td>0.448 00</td>
</tr>
<tr>
<td>O3</td>
<td>0</td>
<td>0</td>
<td>0.448 00</td>
</tr>
<tr>
<td>O4</td>
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<td>(1/2)</td>
<td>0.554 40</td>
</tr>
<tr>
<td>O5</td>
<td>0</td>
<td>0</td>
<td>0.725 10</td>
</tr>
<tr>
<td>C2</td>
<td>(1/2)</td>
<td>(1/2)</td>
<td>0.317 20</td>
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<td>0.671 50</td>
<td>0.296 60</td>
</tr>
<tr>
<td>H5</td>
<td>0.562 80</td>
<td>0.265 80</td>
<td>0.296 60</td>
</tr>
<tr>
<td>H6</td>
<td>0.265 80</td>
<td>0.562 80</td>
<td>0.296 60</td>
</tr>
</tbody>
</table>

\(^\text{a}\) The local symmetry of the CH\(_3\) group does not fulfill the local crystallographic symmetry of 4\(\text{mm}\); thus, the hydrogen positions are disordered. The positions of acidic protons and the hydrogen atoms of the water molecule are not included in the structure model.

(d) \(\text{NH}_3\text{ReO}_4\). The diffraction patterns of "poly-MTO" (1) samples were recorded in asymmetric transmission geometry on a G642 Guinier diffractometer in "step-scanning mode" (counting times, 10–20 s; step widths, \(\theta = 0.005–0.01\); measuring interval, \(\theta = 2–50\)). After 2 days, the first weak reflections originating from \(\text{NH}_3\text{ReO}_4\) were detected. After 4 weeks, no "poly-MTO" reflections at all could be detected. Only very small reflections from single-crystalline, colorless crystals of \(\text{NH}_3\text{ReO}_4\) appeared in the diffraction pattern; tetragonal space group \(I4/\text{a}(\text{no. 88})\); \(a = 5.883(1)\), \(c = 12.980(2)\) Å. Traces of \(\text{NH}_3\) in the laboratory atmosphere were responsible for the slow but quantitative transformation of "poly-MTO" (1) to \(\text{NH}_3\text{ReO}_4\).

(e) "Depolymerization" of MTO. Disk-shaped pressed samples of "poly-MTO" (ca. 150 bar) were measured after single crystals of MTO had grown out of the surface of such samples (approximately 2 weeks).\(^\text{13}\) Reflections belonging to "poly-MTO", ReO\(_3\), and MTO (orthorhombic space group \(\text{Cc}21\) (no. 36); \(a = 7.586(1)\) Å, \(b = 10.426(1)\) Å, \(c = 5.106(1)\) Å) were recorded simultaneously.

(f) X-ray Structure Determination of \(\text{CH}_3\text{ReO}_4\). This compound formed as yellow needles from aqueous "poly-MTO" suspensions (crystal data from ref 20 in brackets): crystal diameters 0.05 × 0.1 × 0.4 mm, monoclinic space group \(\text{Pn}(\text{no. 7})\); \(a = 6.055(2)\), \(b = 8.526(1)\) [8.564(1)], \(c = 9.196(4)\) [9.234(2)], \(\beta = 95.06(2)\) [95.08(2)], \(V = 472\) [479] \(\times 10^6\) pm\(^3\); \(T = 23 ± 1\) °C; \(Z = 2\), \(F(000) = 436\), \(\rho_{\text{calc}} = 3.520\) [3.440] g/cm\(^3\). Ebrah-Nonius CAD4, \(A = 71.07\) pm (Mo Kα, graphite monochromator). The diffraction data were recorded in the same way as described in ref 20. The structure of \(\text{CH}_3\text{ReO}_4\) was solved; it turned out to be isotypic with the previously published structure.\(^\text{20}\)

(g) Neutron Diffraction Study of MTO. The presence of multiple twinning in single-crystals of CH\(_3\)ReO\(_4\) results in unsatisfactory structure refinements using single-crystal X-ray diffraction methods.\(^\text{23}\) The structural model based on single-crystal results was improved using X-ray powder diffraction data and Rietveld analysis. The positions of the deuterium atoms were located by subsequent Rietveld refinements and difference Fourier analyses following neutron powder diffraction measurements (neutron powder diffractometer MAN1/FRM-Garching). However, data were recorded at ambient temperature and sublimation of the MTO sample produced single crystals in the powder samples, resulting in strong preferred orientation effects. For this reason, a definitive low-temperature neutron powder structural study was performed using the high-resolution powder diffractometer (HR-PD)\(^\text{22}\) at the ISIS spallation source (Rutherford Appleton Laboratory, U.K.).

Time-of-flight neutron powder diffraction data were collected at 5 K using a standard "orange" helium flow cryostat on HR-PD. A time-
of-flight diffractometer such as HRPD utilizes a polychromatic neutron beam, and therefore, data are recorded by fixed angle detectors. Neutron wavelengths are discriminated by their time of arrival since \( t = \frac{1}{v} \), \( v \) is the neutron velocity, \( \lambda \) is the neutron wavelength, and \( d \) is the \( d \)-spacing of a particular Bragg reflection. For the present experiments at backscattering, with \( (219) = 168^\circ \), the time-of-flight range used was 30–130 ms, corresponding to a \( d \)-spacing range of between approximately 0.6 and 2.6 Å. Under these experimental settings, the diffraction data have an approximately constant resolution of \( \Delta d/d = 8 \times 10^{-4} \). Data were recorded for a period of ca. 12 h, from a sample of mass ca. 8 g of fully deuterated MTO. Results of the final Rietveld analysis are as follows: orthorhombic space group \( \text{Cmc2}_{1} \) (no. 36), \( a = 7.383 \pm 0.004 \) Å, \( b = 10.310 \pm 0.005 \) Å, \( c = 5.008 \pm 0.004 \) Å, \( V = 381.3 \pm 1 \times 10^6 \) pm\(^3\), \( T = 5 \pm 2 \) K, \( Z = 4 \), \( F(000) = 432 \), \( \rho_{\text{calc}} = 4.396 \) g cm\(^{-3}\), \( R_p = \frac{1}{\Sigma} \frac{(I_{\text{obs}} - I_{\text{calc}})^2}{I_{\text{obs}}} = 3.11 \), \( R_p = \frac{R_p}{1 - R_p} = 1 - 1/(\Sigma I_{\text{calc}}/\Sigma I_{\text{obs}}) = 4.73 \), \( R_p = \frac{\Sigma w \frac{(I_{\text{obs}} - I_{\text{calc}})^2}{I_{\text{obs}}}}{\Sigma w I_{\text{obs}}} \) = 3.74, \( R_p = \frac{\Sigma w I_{\text{obs}}}{\Sigma w I_{\text{calc}}} = 1.67 \), \( \chi^2 = \frac{\Sigma w (I_{\text{obs}} - I_{\text{calc}})^2}{(N - P - 1)} = 5.01 \) for 12 395 observations and 55 basic variables. The observed and calculated diffraction profiles are shown in Figure 16. A small amount of ReO\(_3\) impurity is evident in the fit.

**Figure 16.** Observed (above) and calculated (below) diffraction profiles of MTO.

**Table 3.** Final Coordinates and Equivalent Thermal Displacement Parameters\(^*\) of MTO

<table>
<thead>
<tr>
<th>atom</th>
<th>( x/a )</th>
<th>( y/b )</th>
<th>( z/c )</th>
<th>( U(\text{eq}) ) (Å(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re1</td>
<td>0</td>
<td>-0.172</td>
<td>0.058</td>
<td>0.250 00</td>
</tr>
<tr>
<td>O1</td>
<td>-0.192</td>
<td>-0.105</td>
<td>0.020</td>
<td>0.0086 01</td>
</tr>
<tr>
<td>O2</td>
<td>0</td>
<td>-0.177</td>
<td>0.040</td>
<td>0.0097 01</td>
</tr>
<tr>
<td>C1</td>
<td>0</td>
<td>-0.363</td>
<td>-0.129</td>
<td>0.0081 01</td>
</tr>
<tr>
<td>D1</td>
<td>0</td>
<td>-0.365</td>
<td>0.087</td>
<td>0.0237 01</td>
</tr>
<tr>
<td>D2</td>
<td>0.121</td>
<td>-0.410</td>
<td>-0.209</td>
<td>0.0257 02</td>
</tr>
</tbody>
</table>

\(^*\) \( U(\text{eq}) = \frac{1}{3} \) of the trace of the orthogonalized \( U \).

was placed onto a copper grid. Small crystal fragments or areas of about 2 μm in diameter of crystalline flakes were investigated by selected area diffraction.

Electron diffraction patterns different from that of "poly-MTO" were discovered in only one sample (unpurified sample of 1, prepared at room temperature). They were identified as a crystalline "impurity" with orthorhombic cell constants a = 18.00 Å, b = 13.70 Å, and c = 18.10 Å. The cell constants of this impurity resemble those of α-NbBr₅, which possesses a dimeric structure with two bridging bromo ligands. We suggest a similar dimeric structure consisting of oxo-bridged [(CH₃)₄Re₂O₄]₂ units. (There is also a close structural relationship between (CH₃)₄Re₂O₄ and the corresponding NbC₁₄ tructure.) The anionic trimeric fragment [(CH₃)₄Re₃O₆]⁻ is also found. It is formed from the above (CH₃)₄Re₂O₄ under reduced conditions and in the presence of small amounts of oxygen. The amounts of the as yet unknown impurity must be very small since it was not detectable by X-ray powder diffractometry or any other analytical method, e.g. IR and NMR spectroscopy. However, the impurity has not yet been detected in any other sample prepared at ordinary conditions (ΔT ≧ 70 °C).

(3) Wideline ¹H NMR Spectra. The proton NMR spectra were obtained at 300.1 MHz on a Bruker MSL 300 spectrometer. A background-free ¹H selective probehead with a 5 mm solenoid coil was used. In order to avoid proton signals from a glass (Si-OH) or a Teflon (softeners) sample tube, a lump of the "poly-MTO" or of polycrystalline MTO, respectively, was placed directly into the coil. A proton 90° pulse length of 4 μs was applied, and a dead-time delay of 10 μs was sufficient to exclude ringing effects. The pulse repetition rate was 100 ms. Liquid H₂O served as an external reference (δ = 4.6 ppm). For further details see the caption of Figure 7.

(4) TGA-MS Measurements were performed with a thermobalance TGA 7 (Perkin Elmer) and a mass spectrometer QMG 420 (Balzers) coupled by means of a heated capillary. The samples were subjected to a temperature program with a 2 h segment at 70 °C for drying and a dynamic segment of heating at 10 K/min between 70 and 700 °C. The samples were held in an atmosphere of He (45 sccm, 1 bar).

The samples of compound 1 used in the TGA-MS measurements were freshly synthesized in D₂O (99.3% isotopically enriched). In contrast to the described standard method,¹ compound 1 was washed only with D₂O or H₂O (see the following experimental descriptions) to remove HReO₄.

Experiment a: Compound 1 synthesized and washed with D₂O shows an initial weight loss of 85% (absorbed water) and is followed by a plateau (Figure 17). During a weight loss of 7.6% at 285 °C, one detects intercalated D₂O, CH₄ and CO₂ as well as H₂O (from

![Figure 17](https://example.com/image.png)