

Multiple Bonds between Main-Group Elements and Transition Metals. 138. Polymeric Methyltrioxorhenium: Some Models for Its Electronic Structure

Hugh S. Genin,[†] Kimberly A. Lawler,[†] Roald Hoffmann,^{*,†}
Wolfgang A. Herrmann,^{*,‡} Richard W. Fischer,[‡] and Wolfgang Scherer[‡]

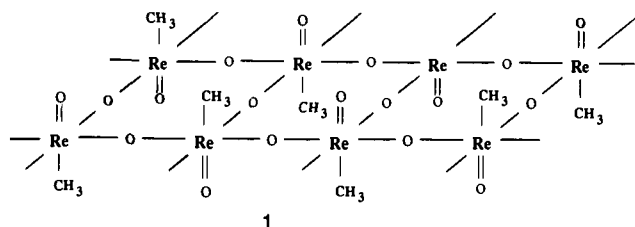
Contribution from Baker Laboratory, Department of Chemistry, Cornell University, Ithaca, New York 14853-1301, and Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

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Abstract: Models of polymeric methyltrioxorhenium (poly-MTO), recently synthesized by Herrmann *et al.*, were investigated by the extended Hückel approximate molecular orbital method. The band structure of poly-MTO resembles that of ReO_3 , but important differences arise from the two-dimensional nature of poly-MTO. The conductivity of poly-MTO can be attributed to occasional demethylation and to the inclusion of extra hydrogen in the lattice. Due to the polymeric nature of poly-MTO, rhenium atoms missing methyl groups are found to be oxidized rather than reduced. A variety of sites for the inclusion of hydrogen in poly-MTO are explored. The H is protonic and, to the extent it is there, provides further reduction of the Re and weakens locally some of the ReO bonds.

While studying the catalytic properties of methyltrioxorhenium(VII) (MTO), Herrmann *et al.* found that when dilute solutions of MTO were left to stand that a gold- or bronze-colored precipitate formed.¹ This powder has a density of 4.38 g cm^{-3} and analyzes as $\text{C}_{0.92}\text{H}_{3.33}\text{ReO}_{3.06}$. It has a resistivity of $6.0 \times 10^{-3} \Omega \text{ cm}$, approximately constant over a wide temperature range. All the carbon is present as methyl groups. The presence of acidic protons in this material has recently been demonstrated by solid state $^1\text{H-NMR}$ spectroscopy.² There may also be some water present, so that the stoichiometry observed is reasonably formulated as $(\text{CH}_3)_{0.92}(\text{H}_2\text{O})_{0.06}(\text{H})_{0.45}\text{ReO}_{3.0}$. Except for the small amount of H_2O and H, the formula is not that different from MTO itself. Yet the molecule is clearly an extended structure and not a monomer.

The extended structure suggested by Herrmann *et al.* for "poly-MTO" (this is what we will call the solid) is shown in 1.



We see a two-dimensional sheet structure. If every Re were to bear a methyl group, the stoichiometry would be that of MTO, CH_3ReO_3 . Approximately one Re in 10 is presumed to be missing a methyl, and there is definitely some excess H in the structure. The CH_3 's are shown alternating above and below the ReO_3 layer; this is just a model, and there is no evidence as yet of this geometrical detail.

[†] Cornell University.

[‡] Technische Universität München.

[⊗] Abstract published in *Advance ACS Abstracts*, February 1, 1995.

(1) Herrmann, W. A.; Fischer, R. W.; Scherer, W. *Adv. Mater.* **1992**, *4*, 653–658.

(2) Herrmann, W. A.; Scherer, W.; Fischer, R. W.; Blümel, J.; Kleine, M.; Mertin, W.; Gruehn, R.; Mink, J.; Boysen, H.; Wilson, C. C.; Ibberson, R. M.; Bachmann, L.; Mattner, M. *J. Am. Chem. Soc.* **1995**, *117*, 3231. Herrmann, W. A.; Fischer, R. W. *J. Am. Chem. Soc.* **1995**, *117*, 3223.

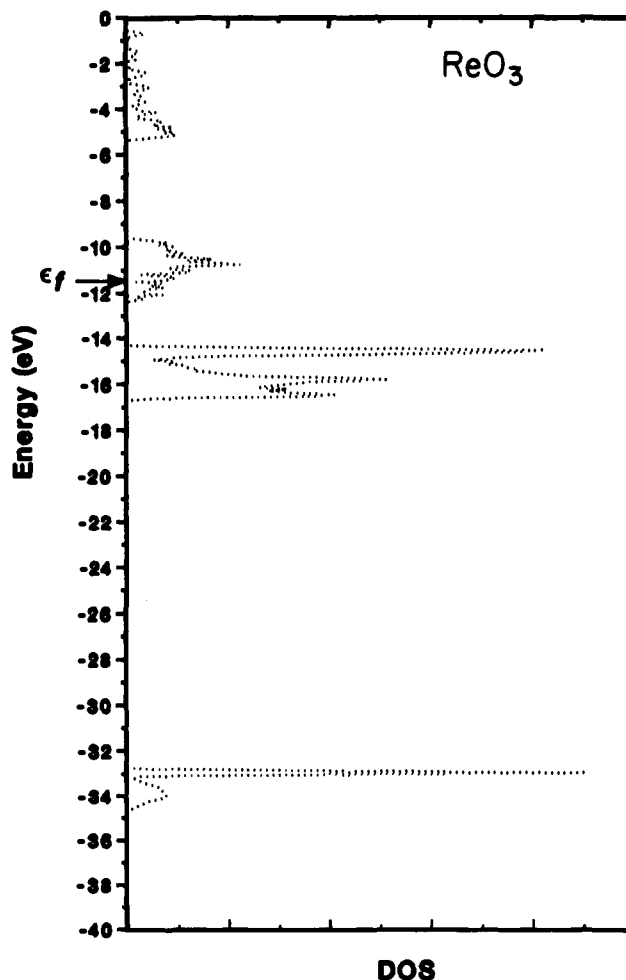


Figure 1. Total density of states of ReO_3 .

The reasonable presumption was that where a methyl was missing one had a locally reduced Re(VI) d^1 center and that the totality of these was primarily responsible for the conductivity (and color) of poly-MTO. The presence of a small number of H atoms would provide further reduction of Re. We

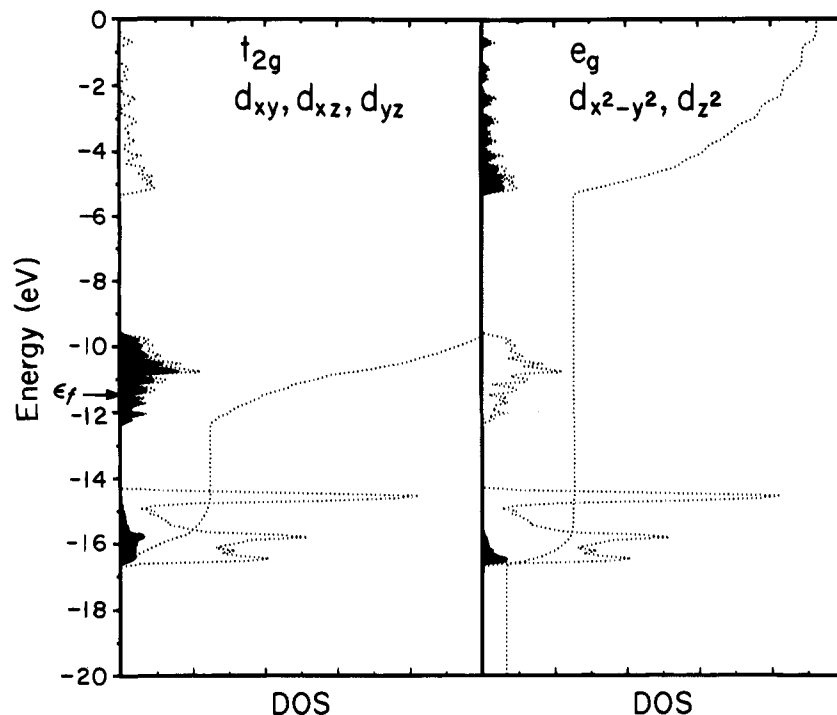


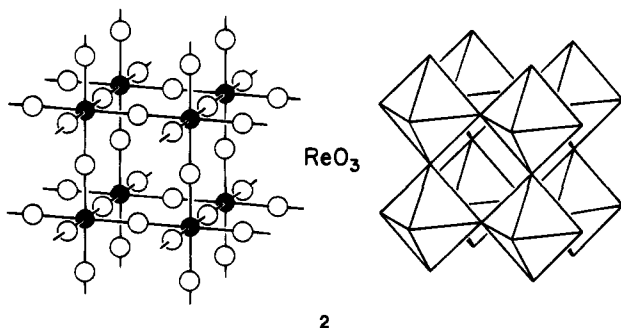
Figure 2. Contributions (solid areas) of the Re t_{2g} (d_{xy} , d_{xz} , and d_{yz}) orbitals (left) and e_g ($d_{x^2-y^2}$ and d_{z^2}) orbitals (right) to the total density of states of ReO_3 . The dotted line is an integration of the DOS contribution on a scale of 0–100% at the top.

undertook a study of the electronic structure of models of poly-MTO, prompted by its interesting electronic properties and the mystery of its structure. As we will see, much of the electronic structure is predictable from what we know of the related ReO_3 ; but, there was a surprise awaiting us in the location of the extra electrons in the extended material.

The calculations used here are of the extended Hückel type, with parameters specified in the Appendix.

ReO₃

The parent structure of poly-MTO is as much the extended ReO_3 solid as the CH_3ReO_3 monomer. It is instructive to look at the former. This beautiful, simple cubic structure with linear oxygens and octahedral rheniums is shown in two representations in 2.



A large energy window density of states (DOS)³ for ReO_3 is shown in Figure 1. Decompositions of the DOS show the expected: the lowest band is mainly O 2s, the next one (between -14 and -17 eV) is O 2p, and the upper two bands are Re 5d. The octahedral crystal field around Re would lead us to expect a typical three (t_{2g}) below two (e_g) crystal field splitting. As the orbital decompositions of Figure 2 show, this is precisely

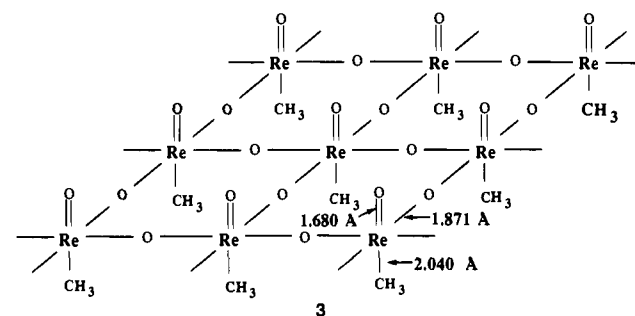
(3) Hoffmann, R. *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures*; VCH: New York, 1988.

what the upper two bands are. For a d^1 system, a portion of the t_{2g} band is filled; this is responsible for the conductivity of ReO_3 .⁴

While these are not relevant to our considerations, note the interesting large “spikes” at the top of the O 2s and 2p bands. These are due to very flat bands, pure oxygen in nature. The presence of such flat bands, called “superdegenerate”, has been discussed in detail in just this ReO_3 structure by T. Hughbanks.⁵

Poly-MTO: All CH₃'s on One Side

The simplest model for poly-MTO is a two-dimensional extended structure with a CH_3ReO_3 composition and unit cell, as shown in 3. For the moment, we will assume that every Re



bears a methyl group and we will neglect the extra hydrogens. The actual system is, of course, three-dimensional. But stacking of CH_3ReO_3 sheets is likely to be governed only by van der Waals contacts, so the two-dimensional model should capture

(4) Previously, ReO_3 , perovskites, and related structures have been discussed in terms of a simple Hückel model: Wheeler, R. A.; Whangbo, M.-H.; Hughbanks, T.; Hoffmann, R.; Burdett, J. K.; Albright, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 2222. For detailed calculations of the electronic structures of ReO_3 and related perovskites, see: Mattheiss, L. F. *Phys. Rev.* **1969**, *181*, 987; *Phys. Rev. B: Condens. Matter* **1972**, *6*, 4718. For comparison of the calculated DOS with XPS findings, see: Wertheim, G. K.; Mattheiss, L. F.; Campagna, M.; Pearsall, T. P. *Phys. Rev. Lett.* **1974**, *32*, 997.

(5) Hughbanks, T. *J. Am. Chem. Soc.* **1985**, *107*, 6851–6859.

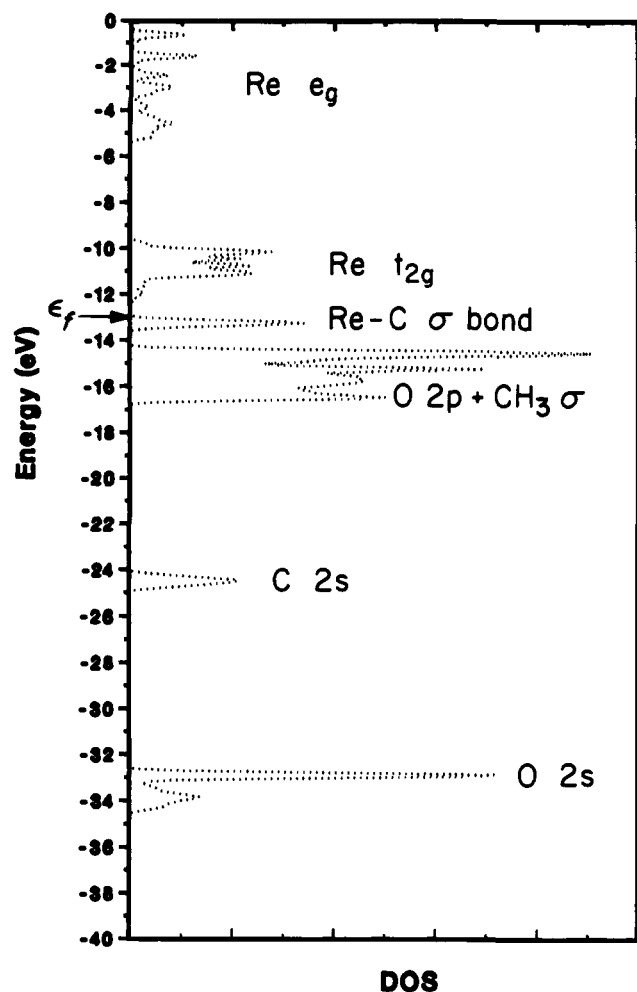


Figure 3. Total density of states of the two-dimensional poly-MTO model 3.

the essential electronic features. In the absence of a complete crystal structure, we chose the in-plane Re–O distance of 1.871 Å from ReO₃ and the out-of-plane Re=O distance of 1.680 Å from the known structure of CH₃ReO₃.⁶ The Re–CH₃ structural parameters also came from the monomer.

Figure 3 shows the total DOS of poly-MTO, model 3. Since this two-dimensional net retains the salient features of the three-dimensional ReO₃ structure, namely the nearly octahedral surrounding of Re (now by five O's and one CH₃), we expect some quite similar features in 3 and ReO₃. Indeed, we see the O 2s and 2p bands and the Re "t_{2g}" and "e_g" bands. The new features are a low-lying C 2s band and the important highest filled band at –13.3 eV, containing C 2p and Re 6s, 6p_z, and 5d_{z²} in a bonding combination, i.e. a Re–C σ bond.

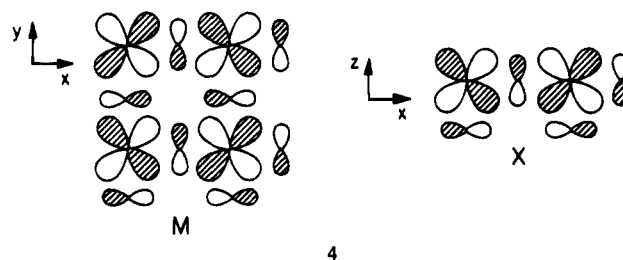
Let us discuss some salient features of these highest occupied and lower unoccupied bands. First the high-lying Re–C σ band. The two electrons in this band are distributed as follows: C, 54%; 3H's, 6%; Re, 20%; O_{terminal}, 10%; O_{in-plane}, 10%. The Re–C crystal orbital overlap population (COOP) curve³ (Figure 4) shows the Re–C bonding nature of this band.

The Re 3d band has several interesting (the comparison is to ReO₃, Figure 2) features: (a) The e_g contribution (0 → –5 eV) partitions (decompositions of DOS are not shown here) into a lower region that is d_{x²–y²} and an upper one that is predominantly d_{z²}. This is due to the stronger axial crystal field of the CH₃ and the axial oxygen, closer to Re than the in-plane O's. (b)

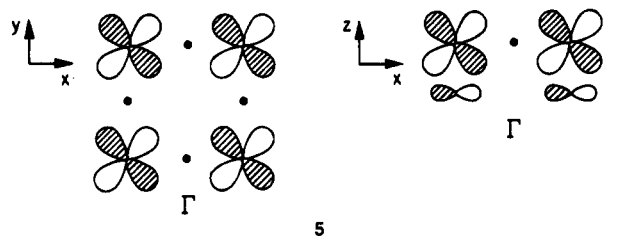
The different shape of the t_{2g} band. The nature of the t_{2g} band is going to be important, so while its significance is not yet clear, we ask the reader to bear with us in the analysis.

The t_{2g} orbitals are the Re d_{xy}, d_{xz}, and d_{yz}. Figure 5 shows the contribution of each to the t_{2g} band. Note that the d_{xy} component is broader than the d_{xz}, d_{yz} pair (nearly degenerate by symmetry). A glance back at ReO₃ will show that the decreased width in the d_{xz} and d_{yz} bands in poly-MTO is the essential difference.

The actual band structure is shown in Figure 6.⁷ Note that d_{xy} is lower (at and near Γ) and higher (at and near M) than d_{xz} and d_{yz}, in different parts of the Brillouin zone. There are two separate reasons for this: (1) First, d_{xy} can participate in maximally four π-antibonding interactions with O 2p's, while d_{xz} (or d_{yz}) can interact in this way with maximally three O 2p's. The relevant combinations that show this at M and X are sketched in 4 (please note the different planes used to show



the orbitals). This is, for instance, the reason d_{xz} and d_{yz} are at lower energy at M than d_{xy}. (2) At Γ, there is no interaction of the d_{xy} with any of the O 2p's (they are of wrong symmetry to interact). The relevant orbitals are shown in 5 at the left. But



the d_{xz} (and d_{yz}) retain the capability of interacting with the axial O 2p (5, right). This destabilizes d_{xz} and d_{yz} relative to d_{xy}. d_{xz} and d_{yz} are also destabilized by the greater interaction that follows from a shorter Re–O_{axial} distance in poly-MTO.

We note finally the total Re–O overlap populations in poly-MTO model 3. They are 0.570 (in plane) and 0.776 (axial). These, of course, reflect the different bond lengths and compare to 0.570 in ReO₃ and 0.872 in the CH₃ReO₃ monomer. That the axial overlap population is quite different from that in CH₃ReO₃, despite an identical bond length, is a reflection of the different π-bonding possibilities in local octahedral (in poly-MTO) vs tetrahedral (in the MTO monomer) coordination.

"Alternating CH₃" Poly-MTO

The title of this section refers descriptively to structure 6, a model poly-MTO, still stoichiometric and still without extra H's, but with CH₃'s (and axial O's) alternately above and below the ReO₂ plane:

(7) Note that the positions of the hydrogens are not known from experimental data; most likely the methyl groups are disordered and/or rotating, neither of which we can simulate in our calculations. We have arbitrarily chosen to orient the methyl group such that a mirror plane exists parallel to the x axis. This arbitrary choice of symmetry results in certain avoided crossings in the band structure (e.g., the d_{yz} and d_{xy} bands in the region between Γ and X) which are artifacts and probably not a characteristic of the real system.

(6) Herrmann, W. A.; Kiprof, P.; Rypdal, K.; Tremmel, J.; Blom, R.; Alberto, R.; Behm, J.; Albach, R. W.; Bock, H.; Solouki, B.; Mink, J.; Lichtenberger, D.; Gruhn, N. H. *J. Am. Chem. Soc.* **1991**, *113*, 6527–6537.

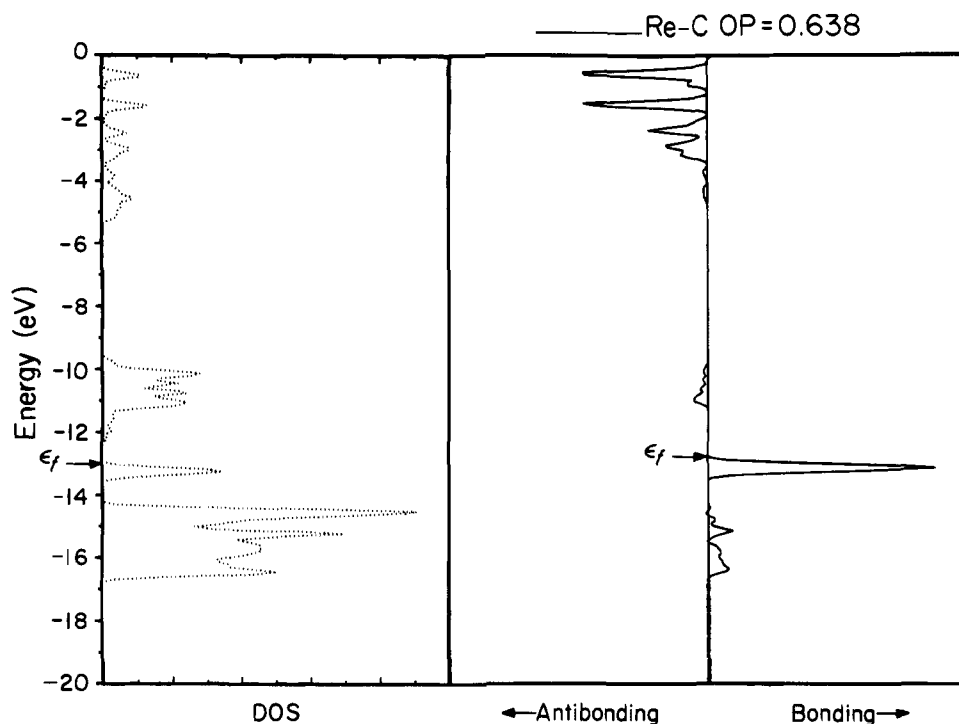
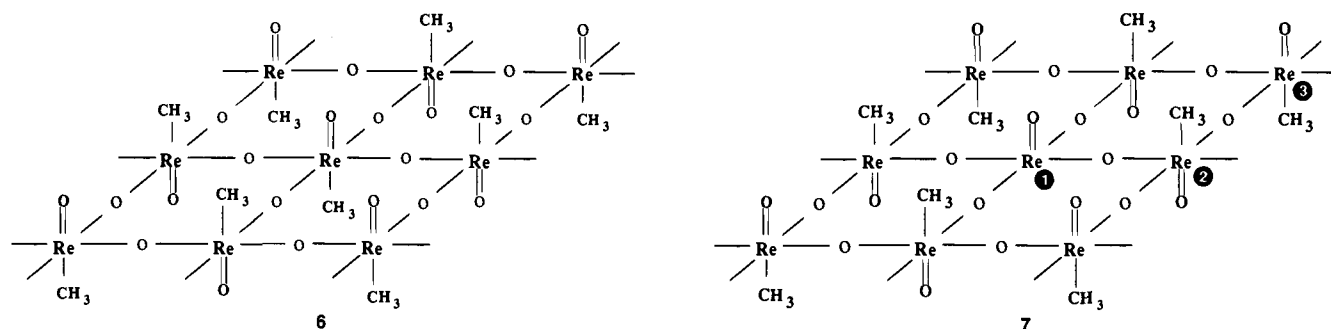


Figure 4. Total density of states (left) and Re–C crystal orbital overlap population (COOP, right) for poly-MTO model 3. Note the strong Re–C bonding in the band just below the Fermi level.



The unit cell of **6** is two times larger than for **3**,⁸ but we would not expect much of a difference, except for possibly some minor through-bond coupling effects.⁹ Indeed, the DOS's of "normal" (Figure 3) and "alternating" (Figure 7, left) poly-MTO (**3** and **6**) are nearly identical. The important broadening of the d_{xy} relative to d_{xz} and d_{yz} bands remains. There is a slight difference in the Fermi level (**6** is higher by 0.05 eV) and stability, the alternating structure being more stable by 0.09 eV per CH_3ReO_3 . We consider this number to be of marginal significance and not necessarily an indicator of the relative stability of the two structures.

$(\text{CH}_3)_{0.75}\text{ReO}_3$: A Partially Demethylated Poly-MTO

It is difficult to model the real composition of poly-MTO, but we want to approach this system step by step, at least its essence of occasional demethylation and protonation and consequent reduction. A convenient first model is the "alternating CH_3 " poly-MTO with one methyl out of four removed, $(\text{CH}_3)_{0.75}\text{ReO}_3$, **7**. Note that we are still neglecting the extra hydrogens found in the real structure.

The DOS of **7** is compared with its precursor, **6**, in Figure 7. The densities of states are nearly identical, except for a single narrow peak (from a corresponding band) at -9.3 eV. This peak is 84% on the demethylated Re: 51%, Re d_{xy} ; 27%, Re

p_z ; 6%, Re s (and small contributions from other orbitals). Clearly this is a hybrid on the demethylated Re, "pointing" toward the vacancy. The resemblance to the orbitals of square pyramidal ML_5 , with their octahedral ML_6 parentage, is obvious.¹⁰

Now for the surprise. One might have thought that the demethylated Re is reduced, for it formally goes from Re(VII), d^0 , to Re(VI), d^1 . But that is not so, and with a vengeance, so to speak. Table 1 compares the calculated electron densities on the demethylated Re (and its remaining axial O) with the intact CH_3ReO units in the structure and with CH_3ReO in the "alternating CH_3 " parent. Note that not only is the demethylated Re not reduced but it is effectively oxidized, losing electrons!

There are two effects at work here. First of all, an extended material is not the sum of its localized constituents. The extra one electron in $(\text{CH}_3)_{0.75}\text{ReO}_3$ does not enter the empty hybrid on the demethylated Re (that is, at -9.3 eV) but the lowest energy orbitals available. Those happen to be the bottom of the Re d_{xy} band, which we so laboriously discussed above. In the extended system, every Re is reduced by demethylation of a few.

But why does the demethylated Re actually lose electrons? This is a subtle point, though easily understood. Consider what is happening as the Re– CH_3 bond breaks, shown schematically in **8**. Initially there are two electrons in the Re– CH_3 bond,

(8) The hydrogens were oriented to preserve the a glide plane.
(9) Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 696.

(10) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

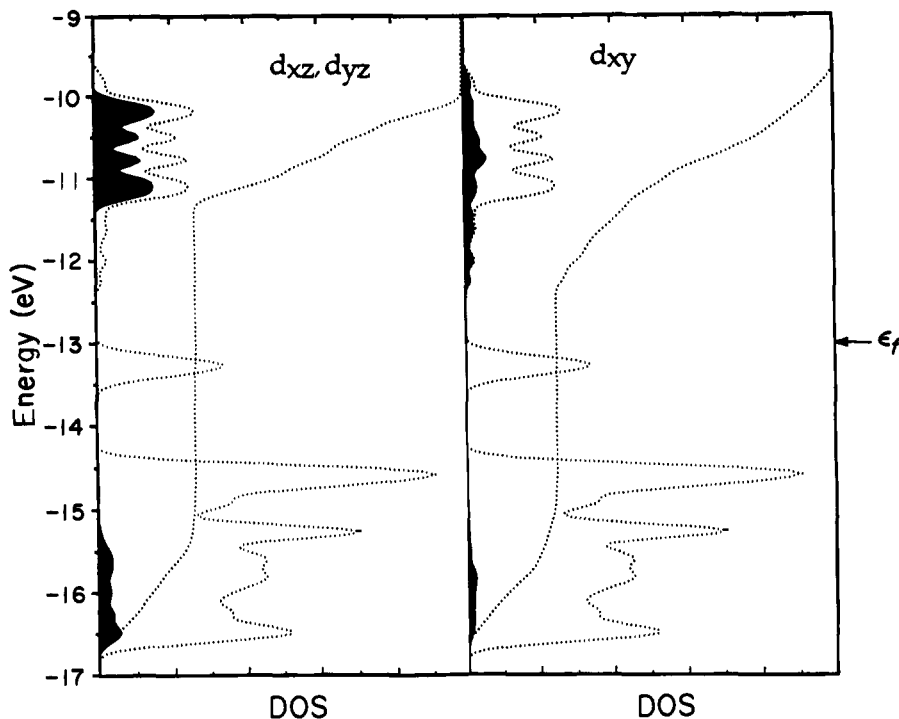
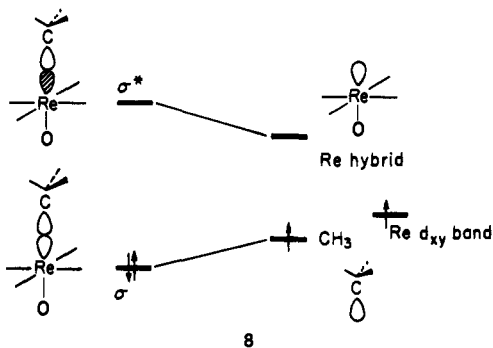


Figure 5. Contributions (solid areas) of the Re d_{xz} and d_{yz} orbitals (together, left) and d_{xy} orbital (right) to the total density of states of poly-MTO model 3. The dotted line is an integration of the relevant orbitals.

Table 1. Selected Electron Densities

	$(\text{CH}_3)_{0.75}\text{ReO}_3$			
	demethylated (site 1) ^a	adjacent (site 2)	across (site 3)	alternating CH_3 poly-MTO
Re	3.71	4.18	4.19	3.97
O	7.01	7.11	7.11	7.11
CH_3		7.29	7.29	7.29

^a "Adjacent" and "across" refer to CH_3ReO units in a square (see 7) in which the demethylated ReO fragment is in one corner; the sites are labeled in 7.



distributed, as we saw, so that the CH_3 has 60% and the Re 20% of the electron density. The bond is assumed to break homolytically, the fate of the CH_3 then being presumably ethane or methane. Anyway, the CH_3 departs with one electron; the remaining electron does not go into the demethylated Re hybrid but into an extended Re network d_{xy} band. As far as the demethylated Re goes, it starts out with 0.41 electrons ($\approx 20\%$ of two electrons) and ends up with (at most) 0.25 electrons (one quarter—there are four Re's per unit cell—of the extra electron in the d_{xy} band). Even its associated axial oxygen is oxidized a little.

The extended Hückel method exaggerates these electron drifts, but the general trend should be correct. A possible test of these considerations might be forthcoming when a detailed structure of poly-MTO becomes available. Here, 9 shows a

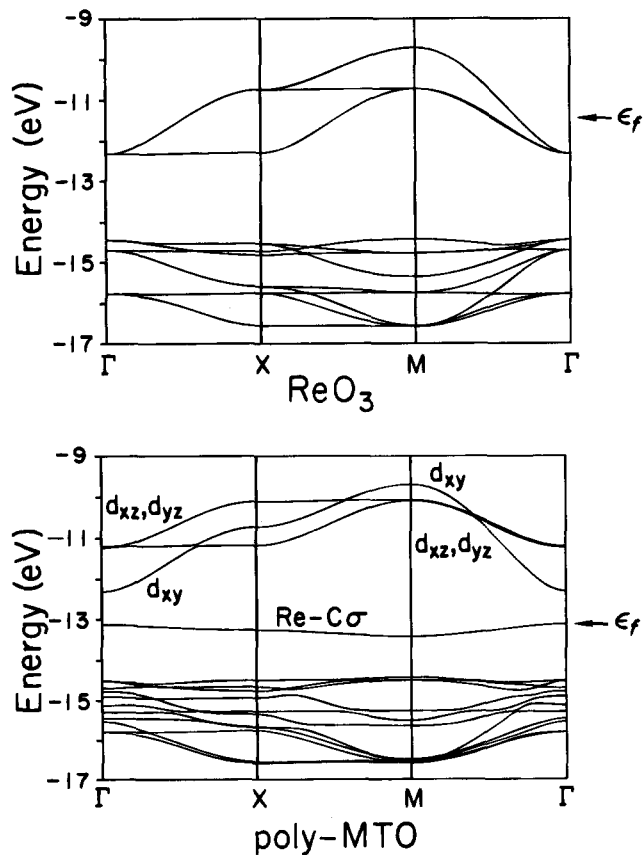


Figure 6. Band structures of ReO_3 (top) and poly-MTO model 3 (bottom).

comparison of the overlap populations in demethylated poly-MTO and the parent system (in parentheses).

Hydrogen in Poly-MTO

Having discussed our model for demethylated poly-MTO, we now turn to the question of the extra hydrogens. The observed

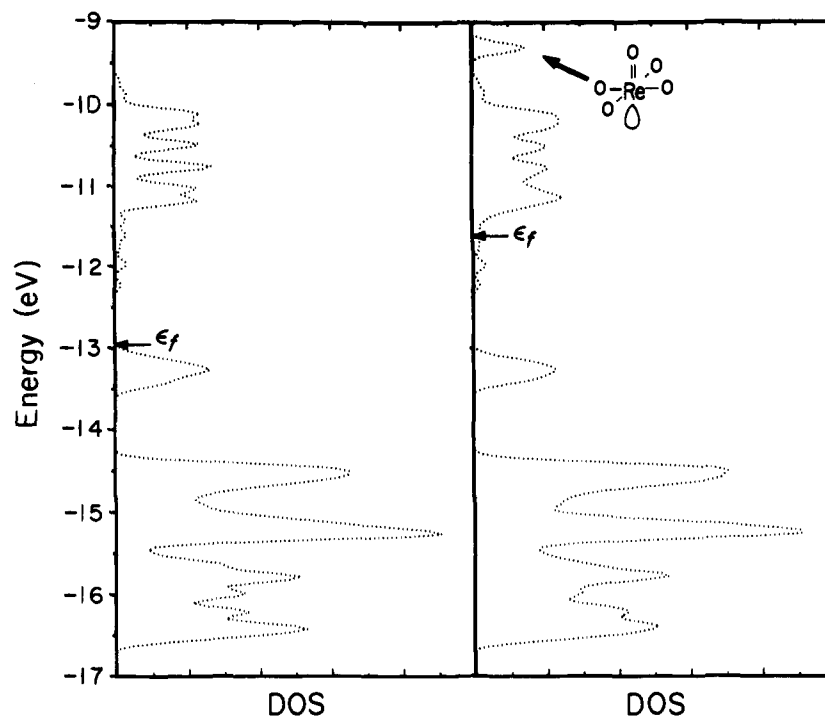
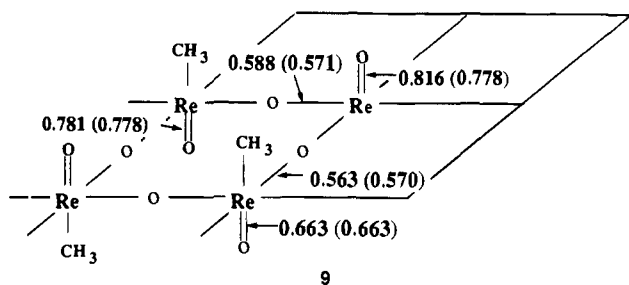


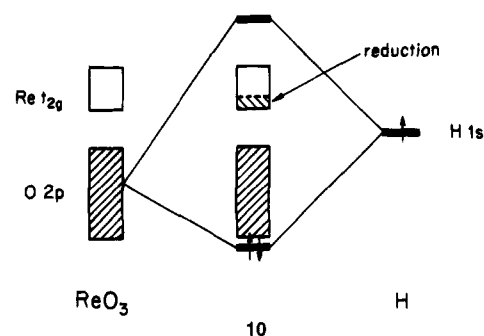
Figure 7. Densities of states of an "alternating CH₃" poly-MTO model 6 (left) and its "partially demethylated" derivative 7 (right).



formula for poly-MTO is $(\text{CH}_3)_{0.92}\text{H}_{0.45}\text{ReO}_{3.0}$, neglecting a small possible amount of water in the solid. Hydrogen insertion in transition metal oxides is not uncommon.¹¹ In particular, hydrogenated ReO_3 bronzes have been synthesized,¹² and Dickens and Weller have solved the structure of $\text{H}_{1.36}\text{ReO}_3$ by neutron diffraction.¹³ $\text{H}_{1.36}\text{ReO}_3$ has a distorted ReO_3 structure, with the extra hydrogens located on the oxygens. There is some tilting of the ReO_6 octahedra in the structure.

Once again, we will look to our parent system, ReO_3 , as a guide. In adding a hydrogen atom to ReO_3 , we would expect to form an O–H σ combination and an O–H σ^* combination from the hydrogen and one of the oxygen lone pairs. This is depicted schematically in 10. The excess electron, originally on H, will not go into the σ^* combination, which is high in energy, but into the lowest available band, one of the Re t_{2g} bands. Thus, by the inclusion of hydrogen in the ReO_3 lattice, we would expect rhenium to be reduced.

We have undertaken a calculation on HReO_3 , which contains one hydrogen per unit cell. We have placed the hydrogen atom arbitrarily on one of the oxygens, within an ReO_2 plane.¹⁴ For



simplicity, we have chosen not to distort the ReO_3 structure as found experimentally. A DOS for HReO_3 (not pictured) reveals that there is some H density in a band at -17 eV, which we identify with the O–H σ bond, localized mostly on the O. The σ^* band lies much higher in energy, well above the Fermi level. As expected, the Re is reduced by hydrogen inclusion in the lattice. The valence electron density on Re goes from 4.55 in ReO_3 to 5.18 in HReO_3 . Note also the rise of the Fermi level, from -11.44 eV in ReO_3 to -11.08 eV.

Now we turn to poly-MTO. A convenient choice of a model system to work with is $\text{CH}_3\text{ReO}_3(\text{H})$, which contains about twice as much hydrogen as the actual structure. There are two obvious choices for hydrogen inclusion. One is to place the hydrogen in the ReO_2 plane on the in-plane O atom, much like the hydrogen position observed in $\text{H}_{1.36}\text{ReO}_3$. The other choice is placing a hydrogen on the axial oxygens.¹⁵ The detailed results are not presented here, but they are consistent with the ReO_3 story. An O–H σ component forms at the bottom of the O 2p

(11) Dickens, P. G.; Weller, M. T. *J. Solid State Chem.* **1983**, *48*, 407. Dickens, P. G.; Weller, M. T. *J. Solid State Chem.* **1985**, *58*, 164. Hibble, S. J.; Dickens, P. G. *J. Solid State Chem.* **1986**, *63*, 154. Ritter, Cl. Z. *Phys. Chem.* **1987**, *151*, 51.

(12) Kimizuka, N.; Akahane, T.; Matsumoto, S.; Yukino, K. *Inorg. Chem.* **1976**, *15*, 3178. Horiuchi, S.; Kimizuka, N.; Yamamoto, A. *Nature* **1979**, *279*, 226.

(13) Dickens, P. G.; Weller, M. T. *J. Solid State Chem.* **1983**, *48*, 407.

(14) This is consistent with the hydrogen positions found in $\text{H}_{1.36}\text{ReO}_3$ (ref 10).

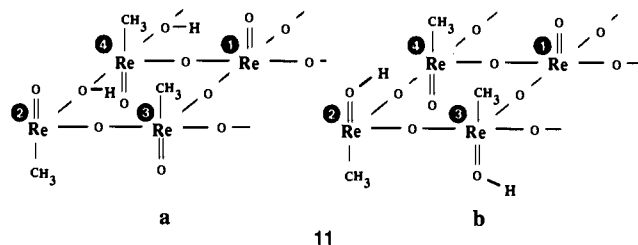
(15) We explored several other choices for hydrogen inclusion on the oxygens. By placing a hydrogen on an in-plane oxygen, we have several different possibilities. The hydrogen can reside such that the O–H axis lies in the ReO_3 plane, perpendicular to the plane (above or below), or in some intermediate position. Calculations on all of these systems yielded almost identical results. For simplicity, and in relation to the HReO_3 structure, we chose the in-plane system. In the case of adding hydrogen to the axial oxygen, there are also several choices for placement of the hydrogen. Calculations on several systems, where the hydrogen was rotated around the Re=O bond, all yielded similar results.

Table 2. Selected Electron Densities and Fermi Levels: Poly-MTO Systems with Occasional Demethylation and Hydrogen Insertion

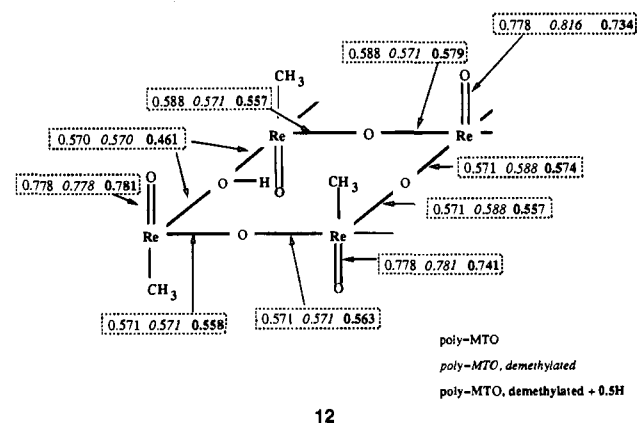
	(CH ₃) _{0.75} ReO ₃	(CH ₃) _{0.75} ReO ₃ (H _{0.5}) (11a)	(CH ₃) _{0.75} ReO ₃ (H _{0.5}) (11b)	(CH ₃) _{0.75} ReO ₃ (H _{0.5}) (H on Re)
Re 1 (demethylated)	3.71	4.54	4.11	3.98
Re 2 (across)	4.19	4.61	4.56	3.97
Re 3 (adjacent)	4.18	4.80	4.72	3.97
Re 4 (adjacent)	4.18	4.78	4.35	3.97
Fermi level	-11.62	-11.17	-11.30	-13.13

band, and a corresponding σ^* band, very high up. There is net reduction of Re, and a little reduction of each O that is not protonated. Energetically, protonation of the axial oxygen is favored by 0.6 eV. However, we do not consider the extended Hückel method to be sufficiently reliable to accurately gauge the relative stability of these two alternative protonated structures.

We move on to models which mimic the effect of occasional demethylation and hydrogen inclusion. Considering once again our demethylated poly-MTO model, alternating ReO₃(CH₃)_{0.75}, which has four Re's per unit cell, we can approach the real stoichiometry by including two hydrogens per unit cell to obtain H_{0.5}ReO₃(CH₃)_{0.75}. If, for the moment, we limit ourselves to placing the hydrogens on oxygen, there are a great number of possible arrangements. Here we will consider just two of these in detail,¹⁶ one with two hydrogens on the in-plane oxygens oriented as in **11a** and one with two hydrogens on the axial oxygens oriented as in **11b**. Some selected results are shown in Table 2. Note the reduction of rhenium and the raising of the Fermi level.



Hydrogen inclusion will also have an effect on bond lengths. In **12** we have depicted the changes in some selected overlap populations on going from idealized poly-MTO, to demethylated poly-MTO (italics), to demethylated poly-MTO with hydrogen (bold). Note the lowering of some of the Re–O overlap



(16) Due to the orientation of the methyl groups and the demethylated rhenium, there are five inequivalent in-plane and four inequivalent axial oxygens in the unit cell. Calculations with the hydrogen on any of the in-plane oxygens (in a variety of geometries) give nearly identical results. Similarly, calculations with hydrogen on any of the three oxygen atoms associated with "methylated" rheniums also give similar results.

populations on going from the demethylated case to the demethylated plus hydrogen case. We hope that some of these differentials in bond strengths can be detected eventually.

As mentioned, demethylating raises the Fermi level and fills the Re t_{2g} band. Hydrogen inclusion raises the Fermi level even higher, effectively putting even more electrons into the Re t_{2g} band. Now we begin to fill regions of the Re t_{2g} band that are higher in energy and have more Re–O antibonding character. Specifically, we begin to fill the narrower d_{xz} and d_{yz} bands, which contribute to Re–O_{axial} π antibonding. This is the reason for the smaller overlap populations for some of the Re–O bonds. Protonation "ties up" some oxygen lone pairs, making them unavailable for π bonding. The protonated O–Re bonds should be significantly longer.

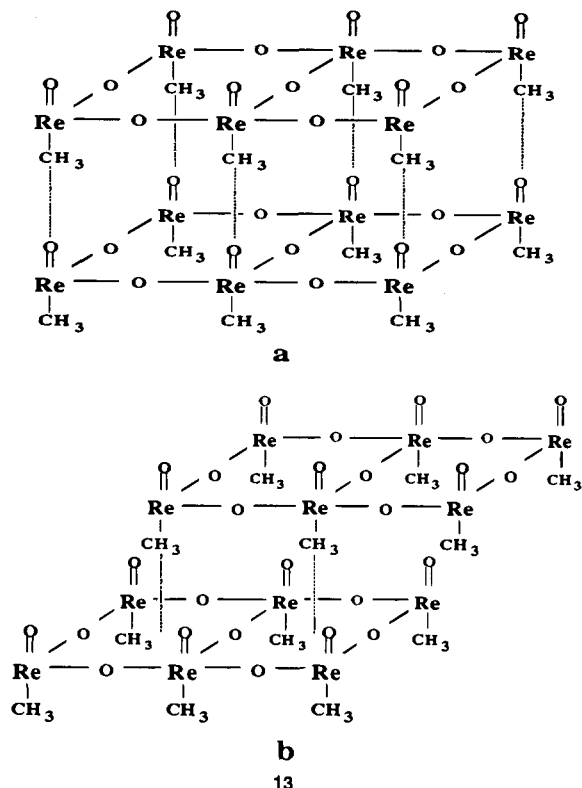
We also carried out a calculation on (CH₃)_{0.75}ReO₃(H)_{0.25}, where the H is placed onto the demethylated rhenium, at an Re–H distance of 1.67 Å.¹⁷ The electronic structure of this system looks very much like idealized poly-MTO. Adding a hydrogen to the demethylated Re essentially "undoes" the effect of demethylation, which was depicted schematically in **8**. The electron from the hydrogen, along with the electron from the delocalized d_{xy} network, goes into a localized Re–H bond. Thus, the hydrogenated Re is reduced and the others are oxidized. Results for this system are also shown in Table 2. Note the similarity to idealized poly-MTO, which has a Re electron density of 3.97 and Fermi level at -13.09 eV.

Poly-MTO in Three Dimensions

Now it is time to bring together our two-dimensional nets to obtain a three-dimensional structure. A convenient way we can accomplish this is simply to take the poly-MTO two-dimensional nets with all the methyl groups residing on the same side, and stack these nets directly above one another, as shown in **13a**. In this arrangement, the terminal oxygens of one net are directly above the methyl groups associated with the adjacent net. An alternative is to stack the nets offset from one another, as in **13b**. In this case, the terminal oxygens of one net are directly above the center of the square formed by four rheniums in the net below. Note that in these calculations we have no missing CH₃'s nor any protonation of oxygens.

We have assembled models of three-dimensional poly-MTO in this way, and we have varied the distance between the Re-containing layers. The total energy per unit cell as a function of distance between layers for model **13a** is indicated by a dotted line in Figure 8. We notice a very flat region down to ≈ 6.5 Å. The energy starts to rise rapidly in the region between 6.5 and 6.0 Å, corresponding to a C_{methyl}–O_{terminal} distance of 2.5 Å. Since the extended Hückel method will not give the expected van der Waals attractive region of the curve, we cannot conclude exactly how far apart the layers should be in this stacking pattern. However, from the repulsive region of the curve, we can estimate the closest reasonable stacking distance. Assuming that a stacking distance leading to a destabilization of more than

(17) Taken from the terminal hydrogens in the structure of Re₂H₈(PEt₂-Ph)₄; Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176.



1 eV would be unreasonable, we would not expect the distance between the layers in poly-MTO model **13a** to be less than 6.0 Å.

What about the alternative model, **13b**? The total energy as a function of the distance between layers for poly-MTO model **13b** is indicated by a solid line in Figure 8. On the basis of this curve, we would not expect the distance between the layers to be less than about 5.5 Å. This corresponds to a $C_{\text{methyl}} - O_{\text{terminal}}$ distance of 3.2 Å but, more importantly, an $H_{\text{methyl}} - O_{\text{terminal}}$ distance of 2.4 Å. The structural considerations of Herrmann *et al.* point to a distance between layers of 6.8 Å. Our theoretical results are certainly consistent with this spacing.

To study the effects of bringing together two-dimensional nets in a slightly different fashion, we opted to bring together sheets of "alternating CH_3 " poly-MTO. In this case, we stacked the "alternating CH_3 " poly-MTO two-dimensional nets directly above one another such that the methyl groups in one layer were directly above the methyl groups in the next layer and terminal oxygens were above terminal oxygens. Results similar to those obtained for model **13a** were obtained. The methyl groups extend out further from the ReO_2 net, so the repulsive interaction begins at a slightly longer distance.

More recently, another model has emerged from experimental studies on poly-MTO in alcoholic aqueous suspensions. In this model, there is what we have called a staggered arrangement of two-dimensional layers. An AA'AA' stacking pattern is assumed, with every other layer juxtaposing O's and CH_3 's. This model has an *average* layer spacing of 8.2 Å, with a water layer intercalated. We have calculated the electronic structure of such a model for poly-MTO as well. The density of states resembles very much those presented above; it shows no new features except the addition of very localized bands arising from the intercalated water molecules.

Lastly, we would like to address the possibility that the extra hydrogens actually reside between the layers. We have tried two models for such a system, the first of which is shown in **14**. With a stacking distance of 6.80 Å, the O-H distance is 1.72 Å (the H is placed symmetrically between the O's). This

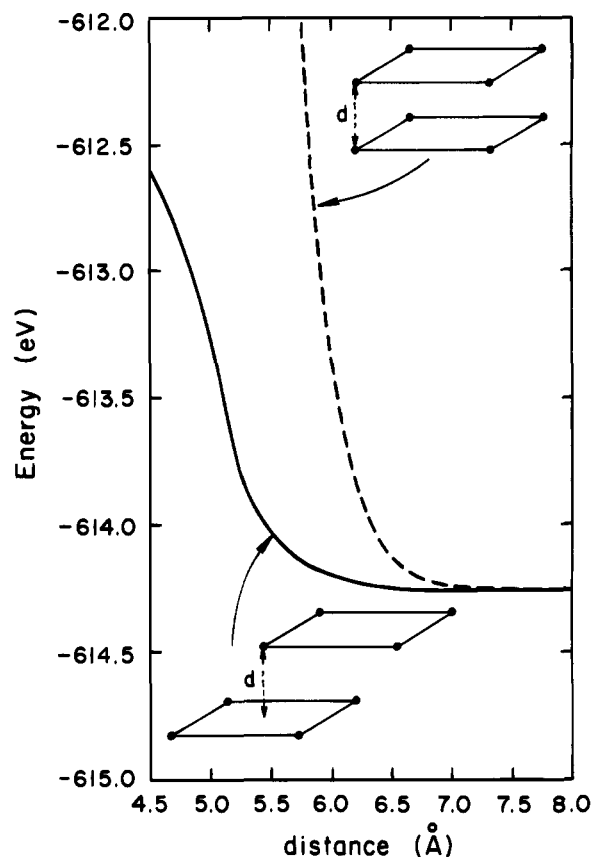
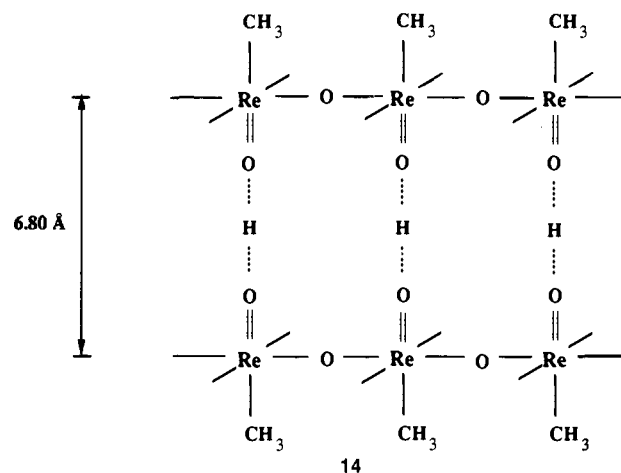
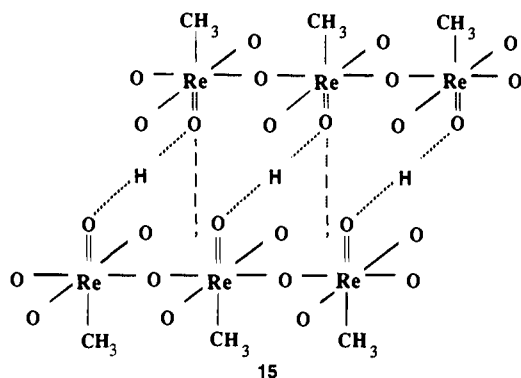


Figure 8. Total energy as a function of separation between ReO_2 layers in a three-dimensional poly-MTO model, **13a** (dotted line) and **13b** (solid line).



is very long; the O-H σ and O-H σ^* bands are not split much. Calculations show that the O-H σ band is at -16.3 eV, in the middle of the oxygen p band; the O-H σ^* band comes at -10.7 eV, about 1 eV above the Fermi level. The Fermi level itself is, as expected, in the bottom of the rhenium band.

The next model for interlayer hydrogen is shown in **15**. Here the two layers are staggered, with axial oxygens from one layer pointing toward a point exactly in-between four Re atoms in the next layer; the hydrogen was placed symmetrically between two axial oxygens from different layers. Interlayer separations were varied such that the O-H distance was between 1.2 and 1.6 Å. The resulting density of states calculations showed O-H σ and σ^* bands which were split more with decreasing bond distance and which were increasingly farther away from the Fermi level. The Fermi level itself was raised, by the contribution of the H 1s electron, into the bottom of the Re d_{xy} band.



Models 14 and 15 have the drawback that they cannot be consistent with both the observed interlayer separation of 6.8 Å and a reasonable symmetric O–H hydrogen bond distance. Calculations were also done on these two models with unsymmetric O–H distances; these resulted in a larger splitting of the bonding and antibonding O–H bands and slightly lower (by <math><1.0\text{ eV/layer}</math>) energy per cell.

While both of these models are plausible, we do not feel that the extended Hückel method can accurately optimize interlayer separations or O–H bond distances. We do not feel we can make any statements about the relative stability of these or the previous models for hydrogen inclusion. Our calculations do reveal, however, that an electrostatic attraction between layers results from the addition of hydrogen. For the case of symmetric O–H bonds, the interlayer hydrogen has an electron density of about 0.6 electrons, while the axial oxygen atoms to either side have 6.8–6.9 electrons, depending on interlayer distance, with the extra charge residing in the p orbitals. Unsymmetric O–H

Table 3. Extended Hückel Parameters

	ζ_i	H_{ii} (eV)	C_1	ζ_2	C_2
Re 6s	2.400	–9.36			
Re 6p	2.370	–5.96			
Re 5d	5.340	–12.66	0.6375	2.277	0.5657
O 2s	2.275	–32.30			
O 2p	2.275	–14.80			
C 2s	1.625	–21.40			
C 2p	1.625	–11.40			
H 1s	1.300	–13.60			

distances result in the hydrogens having again about 0.6 electrons, the H-bonded oxygens having almost no net charge, and the axial oxygens on the layer above having a strong negative charge concentrated in the p, especially the p_z , orbitals.

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Appendix

Extended Hückel calculations were carried out using parameters taken from previous work.¹⁸ These are provided in Table 3. C_1 , C_2 , ζ_1 , and ζ_2 are the coefficients and exponents in a double- ζ expansion of the 5d Slater orbital.

JA9420510

(18) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.