than 1000 $Fe(CO)_5$ molecules are optically thin at this wavelength; so this excitation rate applies to all molecules regardless of their position in the microcrystal. Such a rate is sufficient to excite over 80% of the crystal during the laser pulse. At either laser wavelength this degree of excitation is far more than needed to totally vaporize the crystal into separate $Fe(CO)_5$ molecules or completely reorganize it into an iron cluster plus a rapidly expanding cloud of CO gas. Reorganization is favored in the internal regions of the microcrystal where vaporization is slowed by inertial confinement of the outer layers. Metal cluster growth here competes well with vaporization if the local temperature following absorption of a photon rises above some critical value. For these supersonic microcrystals of $Fe(CO)_5$, such a threshold appears to lie between 2650 and 1930 Å.

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New Layered Compounds with Transition-Metal Oxide Layers Separated by Covalently Bound Organic Ligands. Molybdenum and Tungsten Trioxide-Pyridine

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Layered solid compounds consisting of alternating organic and inorganic layers have recently been of interest in a variety of areas due to their sorptive, catalytic, and transport properties.[1-7] Solids of this type most commonly are formed of negatively charged layers of metal oxide or sulfide and layers of organic cations. Some examples are organoammonium compounds of clay minerals[2] in which the negatively charged inorganic layers are aluminosilicates and the ammonium molybdenum bronzes[3] whose inorganic layers have the double octahedra structure of MoO_3. More recently,[4] it has been recognized that organoammonium ions are also constituents of the organic layer in at least some of the amine intercalates of the transition-metal dichalcogenides.[5] Another series of compounds in which the organic layers are bound in a covalent, rather than ionic, manner to the inorganic layers is the zirconium monoalkyl or monoaryl phosphates and phosphinates in which the organic groups are atttached to the zirconium phosphate layers by P-O-C or P-C covalent bonds.[6] We wish to report new layered compounds of MoO_3 and WO_3 with pyridine and 4,4′-bipyridine that consist of inorganic layers separated by organic layers in which the heterocyclic nitrogen is directly coordinated to the metal atom of the oxide layer. Related materials in which a coordinated organic ligand separate planar inorganic layers are the nickel cyanide complexes $NiL_2Ni(CN)_4$.[7]

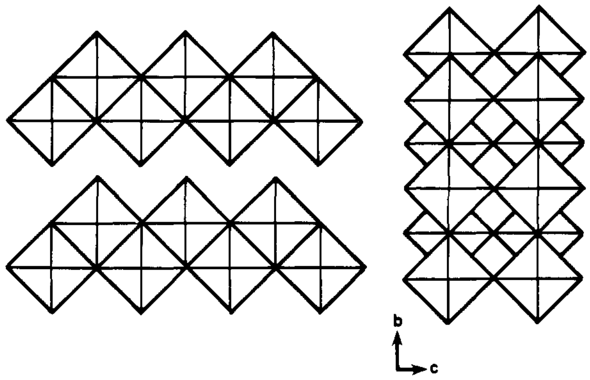

Figure 1. Two views of the structure of MoO_3. The layers are formed of MoO_6 octahedra that are connected by μ^2 oxygens along *c* and by μ^3 oxygens along *b*. The layers are stacked along *a* and held together by van der Waals contacts of terminal oxygens.

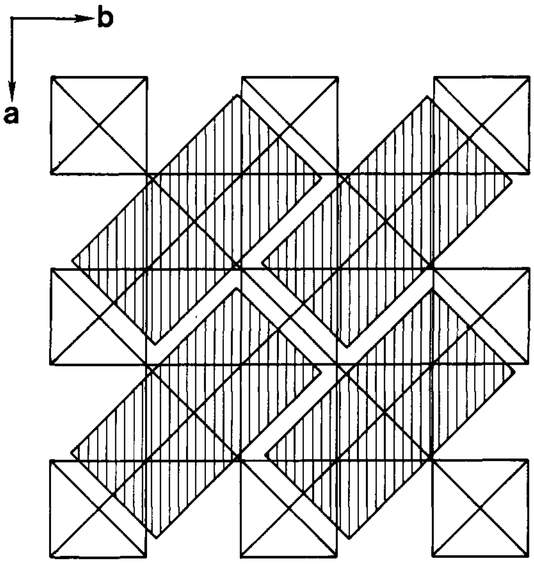

Figure 2. View of the structure of $MoO_3C_5H_5N$ looking down *c* upon the layers. The shaded rectangles represent the van der Waals dimensions of the pyridine molecule. To conform to the observed tetragonal symmetry, the pyridine molecules must be disordered by a 90° rotation around the Mo-N bond.

MoO_3 consists of 6.928-Å thick double layers of edge- and corner-sharing octahedra represented by the formula $MoO_{1/1}O_{2/2}O_{3/3}$,[8] as depicted in Figure 1. When excess pyridine is heated with MoO_3 under strictly anhydrous conditions, microcrystalline $MoO_3C_5H_5N$ is formed.[9] Infrared[11] and structural data (vide infra) demonstrate that pyridine is directly coordinated

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[8] Hulliger, F. "Structural Chemistry of Layer-Type Phases"; Reidel, D.: Boston, 1976; p 169 ff. The structural formula $MoO_{1/1}O_{2/2}O_{3/3}$ indicates the Mo is octahedrally coordinated by 1 unshared oxygen ($O_{1/1}$), two O atoms shared with another Mo ($O_{2/2}$), and three O atoms shared with two other Mo ($O_{3/3}$). In organometallic notation, the Mo coordination sphere would be represented by $MoO(\mu^2\text{-}O)_2(\mu^3\text{-}O)_3$.

[9] Elemental analysis (C, H, N, Mo) and TGA confirmed the stoichiometry. The synthesis is tedious. Prolonged heating (30 days) at 160-180 °C in sealed tubes with intermediate regrinding is necessary to ensure complete reaction of the MoO_3. The compound has been previously reported[10] but not structurally characterized.

[10] Bernard, J.; Camelot, M. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1966**, *263*, 1068-1071.

[11] IR (cm^{-1}, intensity): 1644 w, 1603 s, 1573 m, 1540 vw, 1486 m, 1443 vs, 1239 w, 1220 m, 1156 vw, 1141 m, 1062 s, 1041 s, 1012 vw, 1004 vw, 950 w, 931 vs. This spectrum best fits known spectra of pyridine coordinated to a metal atom (Lewis base) site.[12] Particularly, an intense band at ca. 1542 cm^{-1} characteristic of pyridinium ion is almost totally absent.

[12] Matulewicz, E. R. A.; Kerkhof, F. P. J. M.; Moulijn, J. A.; Reitsma, H. J. *J. Colloid Interface Sci.* **1980**, *77*, 110-119. Perry, E. P. *J. Catal.* **1963**, *2*, 371-379.

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to the molybdenum atom. Accurate X-ray powder data[13] can be refined to a tetragonal unit cell of dimensions $a = 5.271$ (2) and $c = 11.477$ (4) Å. The intensity patterns of partially oriented specimens indicate that the c axis corresponds to the layer repeat distance. The observed increase in layer spacing (4.55 Å) can be used in conjunction with the known MoO_3 layer area (14.65 $Å^2$/Mo atom) to calculate an increase in interlayer volume of 67 $Å^3$ per 2Mo, assuming the MoO_3 double layers remain intact. However, since the volume of a pyridine molecule is 134 $Å^3$, the observed composition of $MoO_3C_5H_5N$ would require 268 $Å^3$ of additional interlayer volume if a structural model retaining the original MoO_3 double layers were correct.[14] We therefore conclude that the structure of the MoO_3 layers has been completely changed. We propose a new model for the molybdenum oxide layers that is consistent with the X-ray, infrared, and compositional data. In this model, the molybdenum atoms are octahedrally coordinated by five oxygens and a pyridine nitrogen atom. Four of the oxygen atoms are in the equatorial plane of the Mo octahedron and bridge to other Mo atoms. A fifth oxygen is unshared, forming a molybdenyl group. The pyridine is coordinated trans to this molybdenyl oxygen, resulting in a structural formula $MoO_{1/1}O_{4/2}(C_5H_5N)_{1/1}$. The resulting lattice fits the observed lattice parameters well if one assumes the Mo=O and Mo–N bonds alternate regularly on the 001 planar surface and that the pyridine is disordered around the Mo–N axis as indicated in Figure 2. The model is similar to the known structure $MoO_3{\cdot}2H_2O$[8] which consists of $MoO_{1/1}O_{4/2}(H_2O)_{1/1}$ octahedra and uncoordinated interlayer water molecules. $MoO_3{\cdot}2H_2O$ has a monoclinic unit cell that is slightly distorted from the ideal tetragonal cell, but the average separation between octahedra of 3.73 Å agrees precisely with that calculated from the model structure and the observed a axis in $MoO_3C_5H_5N$.[15] The interlayer separation c is more difficult to predict because it is determined by van der Waals contacts of H atoms in the 3 position in pyridine molecules coordinated to adjacent layers, but it is in the expected range derived from typical Mo–N bond lengths and the van der Waals size of pyridine molecules. As is exhibited in Figure 2, the coordinated pyridine molecules efficiently fill the available area on the layer surfaces.

We have also synthesized the structurally isomorphous tungsten analogue $WO_3C_5H_5N$ by heating H_2WO_4 with pyridine in the presence of molecular sieves to remove the evolved water.[16] The X-ray pattern is almost identical with that of $MoO_3C_5H_5N$ except for intensity differences due to the greater scattering power of tungsten. The only significant difference in the infrared spectra is the strong band at 947 cm^{-1} which is observed at 931 cm^{-1} in $MoO_3C_5H_5N$. We assign this band to the M=O stretch and the higher frequency bands to pyridine vibrations.

The metal oxide layers can be covalently connected by employing 4,4′-bipyridine as the ligand. The resulting compound, $MoO_3(bpy)_{0.5}$[17] has lattice parameters $a = 5.265$ (2) $c = 22.760$ (5) Å and absences indicate a body centered cell. The 001 layer reflections are present only for $l = 2n$, indicating the layer spacing is $c/2 = 11.38$ Å. This value compares favorably with the Ni-bpy-Ni distance in the bis[(difluoroboron)dimethylglyoximato]nickel-4,4′-bipyridine adduct of 11.78 Å.[18] The structural relation between $MoO_3C_5H_5N$ and $MoO_3(bpy)_{0.5}$ is displayed in Figure 3.

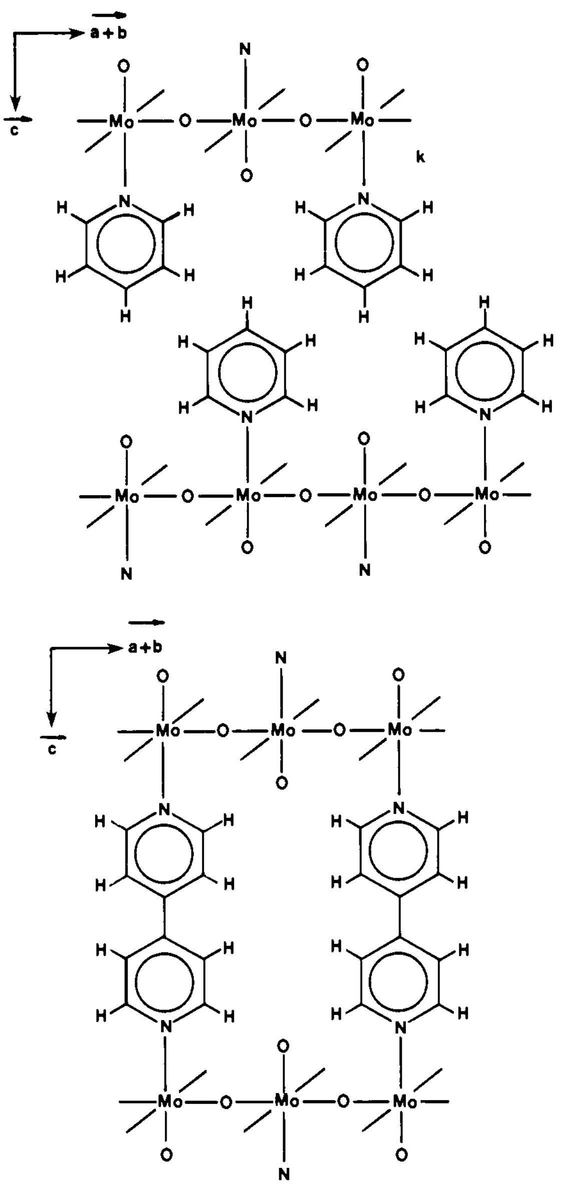

Figure 3. Relation of the structures of $MoO_3C_5H_5N$ (top) and $MoO_3(bpy)_{0.5}$ (bottom). The view is parallel to the layers.

$MoO_3C_5H_5N$ decomposes cleanly at 250 °C to MoO_3 and pyridine in either a He or a dry O_2 atmosphere. The evolved pyridine can be trapped and identified by IR and NMR spectroscopy. $WO_3C_5H_5N$ is more stable, decomposing at 340 °C. Cross-linking the layers with organic pillars has a dramatic effect on compound stability, as $MoO_3(bpy)_{0.5}$ decomposes at 400 °C.

Thus, we have prepared and characterized a series of unique stoichiometric compounds in which infinite two-dimensional molybdenum or tungsten oxide layers are separated by directly coordinated pyridine ligands. Following the structural principle of linking inorganic layers by coordination of metal atoms in the layers to rigid bridging organic ligands, a wide range of new compounds of potential interest can be envisioned.

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(13) X-ray data were collected on a Philips powder diffractometer by using Cu Kα radiation. Thirty six well-defined diffraction maxima were observed at $2\theta < 70°$. The position of 22 maxima ($2\theta > 30°$, KCl internal calibrant) were used to refine unit cell parameters. No unindexable maxima were observed. The measured density (displacement in Fluorochemical FC77) of 2.30 g cm^{-3} agrees well with the density calculated from the unit cell dimensions for $Z = 2$, 2.32 g cm^{-3}.

(14) In contrast, the known molybdenum bronze $H_xMoO_3(C_5H_5N)_{0.3}$[3] has a layer spacing of 12.88 Å corresponding to an increase in interlayer volume of 88 $Å^3$/2Mo, which allows the incorporation of 0.3 equiv of pyridine of volume 80 $Å^2$/2Mo.

(15) For $MoO_3{\cdot}2H_2O$ $(a + c)/(4\sqrt{2}) = 3.727$ Å. For $MoO_3C_5H_5N$ $a/\sqrt{2} = 3.727$ Å.

(16) WO_3 and pyridine do not react at temperature up to 230 °C. Heating H_2WO_4 and excess pyridine for 7 days at 150 °C in the presence of molecular sieves results in pale yellow green $WO_3C_5H_5N$. Lattice parameters $a = 5.296$ (4), $c = 11.488$ (10). IR: 1647 vw, 1605 s, 1572 w, 1488 w, 1446 vs, 1239 vw, 1220 w, 1159 vw, 1141 w, 1063 m, 1042 m, 1006 vw, 947 s cm^{-1}.

(17) $MoO_3(bpy)_{0.5}$ was synthesized by heating excess bpy in xylene with MoO_3 for 16 days at 250 °C. The particle size was reduced after 11 days by grinding the intermediate product in a McCrone micronizing mill. The formula was confirmed by elemental analysis and TGA.

(18) Stephens, F. S.; Vagg, R. S. *Inorg. Chim. Acta* **1980**, *42*, 139–143. The model for $MoO_3(bpy)_{0.5}$ does not require the Mo to be at the center of its octahedron. In fact, we would expect it to be displaced ~0.2 Å along z toward the molybdenyl oxygen, thus making the observed $c/2$ about 0.4 Å shorter than the actual Mo–bpy–Mo distance.