Polymeric Complexes from Molybdenum Trioxide, with Notes on Derivatives and Related Compounds

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Molybdenum trioxide dissolves in dimethyl sulphoxide (dmso) to give a solution from which the polymeric complex $[\{MoO_3(dmso)_{1.33}\}_n]$ (1a) may be crystallised. It also reacts with pyridine *N*-oxide (pyo), triphenylarsine oxide, and pyridine (py) to give insoluble polymeric complexes $[\{MoO_3(pyo)\}_n]$ (2), $[\{MoO_3(AsPh_3O)_{0.5}\}_n]$ (3), and $[\{MoO_3(py)\}_n]$ (4). The solubility of (1a) enables its conversion to (2), (3), or (4). Another compound, $[\{MoO_3(AsPh_3O)\}_n]$ (5) has been obtained from the Mo^{VI} acetylacetonate complex $[MoO_2(acac)_2]$. Evidence on the constitution of the insoluble compounds comes from i.r. spectra and *X*-ray diffractograms, with the ' white ' and ' yellow ' molybdic acids, $[\{MoO_3(OH_2)\}_n]$ and $[\{MoO_3(OH_2)\}_n]\cdot nH_2O$ respectively, providing reference structures. The molybdenum co-ordination environment comprises the ligand opposite a single terminal oxygen, along with four bridging atoms, as in the yellow form of the acid. The formation of these compounds is considered in relation to the simpler Mo–O–Mo bridge-cleavage reaction shown by the ' digol ' compound $[\{MoO_2(deg)\}_n]$ (H_2deg = diethylene glycol), to give complexes of the type $[MoO_2(deg)L]$. Solutions of (1a) react with hydroxylic compounds in the presence of triethoxymethane as condensing agent. Products obtained from 2-amino-2-methylpropane-1,3-diol and 2-hydroxymethyl-2-methylpropane-1,3-diol are reported.

Six-fold co-ordination around molybdenum(VI) is attained through use of varied combinations of core oxygen atoms and ligand oxygen, O_l. There is usually considerable asymmetry within the co-ordination sphere, arising predominantly from a lengthening of the bonds to atoms which lie *trans* to the short bonds (*ca.* 1.67—1.71 Å) to terminal oxygen, O_t. There is also the special case where strongly bonded oxygen atoms, which might be described as terminal-bridging, O_{tb}, are weakly co-ordinated with adjacent molybdenum centres to form an almost linear Mo–O · · · Mo–O · · · chain with highly asymmetric bridges (Mo–O *ca.* 1.7 and 2.3 Å). Both the usual *trans* effect and O_{tb} bridging are shown in crystalline molybdenum trioxide.[1,2] Similar asymmetric bridging also occurs in the ' digol ' complex, $[\{MoO_2(deg)\}_n]$ (where *n* is large), from diethylene glycol (H_2deg).[3]

The structure of molybdenum trioxide, and the molybdenum co-ordination environment are shown in Figure 1, from the work of Kihlborg.[2] The structure contains zig-zag chains of edge-sharing octahedra, as in the sequence A, B, C . . . . Symmetrical bridges between alternate molybdenum centres extend through O(2) and O(2′) in the direction of the *c* axis. These chains of octahedra are linked laterally through corner-sharing of the atoms O(3) and O(3′), which form a sequence of alternating strong and weak bonds in the direction of the *a* axis. There are thus long weak bonds to O(3′) and to the triple-bridging O(4) opposite the terminal oxygen O(1) (Figure 1). (For such structures, the Mo–O bond order in relation to bond length has been discussed by Cotton and Wing,[4] and by Schröder.[5]) There seemed the possibility that one or both of these weak bonds might be broken through insertion of sufficiently strongly electron-donating ligands. The structural similarity of ' white molybdic acid,' $[\{MoO_3(OH_2)\}_n]$,[6] to molybdenum trioxide can be regarded as an example of the result of such a conversion, with the breaking of the Mo–O(3′) bond in the oxide allowing co-ordination of a water molecule.

It is found that the compound $[\{MoO_2(deg)\}_n]$[3] gives a reaction in which there is this kind of simple bridge cleavage. But the formation of new derivatives from the trioxide also involves a breaking of Mo–O(4), through rearrangement of the molybdenum–oxygen framework to give layer structures of the kind in ' yellow molybdic acid,' $[\{MoO_3(OH_2)\}_n]\cdot nH_2O$.[7]

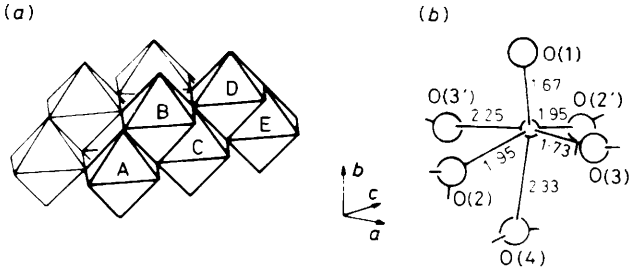


Figure 1. (*a*) Arrangement of octahedra in molybdenum trioxide. (*b*) The molybdenum environment in the B and D octahedra with bond lengths Å (see ref. 2)

Results and Discussion

Molybdenum trioxide dissolves slowly in dimethyl sulphoxide (dmso) at temperatures above 120 °C to give a solution from which two crystalline phases, both of formulation $[\{MoO_3(dmso)_{1.33}\}_n]$ (1a) and (1b), may be obtained. The crystal structure of (1a) has recently been determined by McCarron and Harlow[8] who showed the compound to be a chain polymer with a sequence of two octahedral and one tetrahedral molybdenum centres. The i.r. spectrum of (1b) indicates a close similarity, with significant differences only in the Mo–O–Mo bridging region, 800—720 cm^{-1} (Table 1).

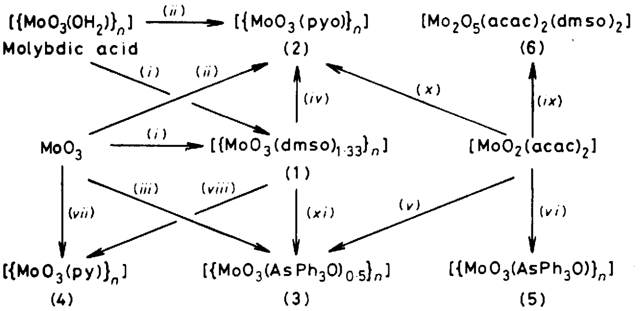
The trioxide also reacts with pyridine *N*-oxide (pyo), triphenylarsine oxide, and pyridine (py) to form the insoluble complexes $[\{MoO_3(pyo)\}_n]$ (2), $[\{MoO_3(AsPh_3O)_{0.5}\}_n]$ (3), and $[\{MoO_3(py)\}_n]$ (4). The solubility of (1a) (in dmso or ethanol) is favourable to ligand exchange, as in the conversions to (2), (3), and (4) shown in Scheme 1, and to condensation reactions (see below).

Scheme 1 includes reactions using molybdenum(VI) acetylacetonate (acac) complexes; $[MoO_2(acac)_2]$ can be converted to (2) and (3), providing there is access of atmos-

Table 1. Infrared bands (cm^{-1})

Compound	$\nu(\text{Mo-O}_t)$	$\nu(\text{Mo-O-Mo})$	$\nu(\text{Mo-O}_l)$	$\nu(\text{X-O})$ [a]
(1a) $[\{MoO_3(dmso)_{1.33}\}_n]$	950m, 930m, 900s, 888s	758s, 665s br	(560sh), 430m [b]	1 015s, 995m
(1b) $[\{MoO_3(dmso)_{1.33}\}_n]$	950m, 926s, 898s, 885s	(730w), 655s br	455m	1 015s, 1 000s
(2) $[\{MoO_3(pyo)\}_n]$	898s, (943m) [c]	745—730m [d]	580s, 550s [e]	1 204s
(3) $[\{MoO_3(AsPh_3O)_{0.5}\}_n]$	958s	900—750m [f]	500—450m br	805s
(4) $[\{MoO_3(py)\}_n]$	933s	725vs, 640—630vs	[g]	—
(5) $[\{MoO_3(AsPh_3O)\}_n]$	909s, (930m) [c]	710—680m, 660s	570s	870s, 845m
(6) $[Mo_2O_5(acac)_2(dmso)_2]$	930s, 905—895s	775s	555w, 440m [b]	1 580s, 1 520s (C=O); 1 000s (S=O)
(7) $[\{MoO_2(deg)\}_n]$ [3,8]	912s, 847s br [h]		590s, 560w	1 085s, 1 055s, 1 020s (C–O)
(8) $[MoO_2(deg)(dmso)]$	920s, 910s	—	567s, 555m, 435w [b]	1 086s, 1 058s, 1 020s (C–O); 1 008s (S=O)
(9) $[MoO_2(deg)(py)]$	915s, 905s	—	560s, 548m	1 089s, 1 055s, 1 020s (C–O)
(10) $[MoO_2(amp)(dmso)]$ [i]	920s, 900s	635s [j]	533m, 520s	1 108s, 1 078s, 1 040s (C–O); 1 010s (S=O)
(11) $[(MoO_2)_2(amp)(Hamp)_2]$	912s, 863s [k]	708s,[l] 682s [l]	573s, 530s	1 068s br, 1 030s (C–O, C–N)
(12a) $[\{MoO(hmmp)(OEt)\}_n]$ [m]	940s	620s, 607w	557s	1 130s, 1 085w, 1 065s, 1 045s, 1 020w, 996s, 980m (C–O)
(12b) $[\{MoO(hmmp)(OEt)\}_n]$ [m]	940s	633s,[j] 606s [j]	560m	1 128s, 1 090m, 1 068w, 1 040m, 1 010m, 997w, 970m (C–O)
(13) $[\{(MoO_2)_2(hmmp)(OEt)\}_2]$ [17]	950s, 938m, 920m, 905s	650ms,[j] 620ms [j]	568s,[n] 510s [n]	1 105s, 1 032s, 988 (C–O)
MoO_3	980s, 865s br [h]	590s, 570s, 520m		
$[\{MoO_3(OH_2)\}_n]$	970m, 914s br [o]	600s br, 530m		
$[\{MoO_3(OH_2)\}_n]\cdot nH_2O$	970m, 905mw	775(sh), 745s br, 665s br		

[a] X = N, S, As, or C (where shown). Listing of ligand bands is limited to these categories. [b] Band at 440—430 cm^{-1} characteristic of co-ordinated dmso. [c] Unassigned medium-intensity band in the $\nu(\text{Mo-O}_t)$ range. [d] Strong bands at 840 and 770 cm^{-1} are coincident with ligand absorptions. [e] A ligand band at this frequency is strongly enhanced. [f] Upper limit of bridging band uncertain. [g] Assignment of $\nu(\text{Mo-py})$ uncertain. [h] Band characteristic of O_{tb} type bridging. [i] Compound is probably dimeric. [j] Ligand bridge bands, typically below 650 cm^{-1}. [k] May correspond with a ligand band at 875 cm^{-1}. [l] It is probable that this bridging is through each of the oxygen atoms of the dianion amp. [m] Isomeric compounds. [n] Could also involve the triple-bridging oxygen atoms.[19] [o] Broadening, without displacement to lower frequency, may be associated with the triple-bridging O_b *trans* to one of the O_t atoms.



Scheme 1. (*i*) dmso, dissolves slowly at 120 °C; (*ii*) pyo, in chlorobenzene at 125 °C; (*iii*) $AsPh_3O$, in bromobenzene under reflux; (*iv*) pyo, precipitation from ethanol; (*v*) $AsPh_3O$, precipitation from ethanol in air to provide moisture; (*vi*) $AsPh_3O$, precipitation from benzene; (*vii*) pyo, prolonged reflux with pyridine; (*viii*) py, under reflux; (*ix*) dmso, precipitation from ethanol in air to provide moisture; (*x*) pyo, precipitation from ethanol in air to provide moisture; (*xi*) $AsPh_3O$, precipitation from ethanol

pheric moisture, but the products are contaminated with molybdenum trioxide. The reaction of $[MoO_2(acac)_2]$ with $AsPh_3O$ in benzene yields a second polymeric complex from this ligand, of stoicheiometry approaching $[\{MoO_3(AsPh_3O)\}_n]$ (5), which was not obtainable from the trioxide. Reaction of $[MoO_2(acac)_2]$ with dmso causes displacement of only one mole of ligand to give a crystalline product $[Mo_2O_5(acac)_2(dmso)_2]$ (6). This compound shows a Mo–O–Mo core-bridging band at *ca.* 780 cm^{-1} characteristic of the Mo_2O^5 unit.[9]

In the two $AsPh_3O$ complexes (3) and (5) the role of the ligand differs. In (5) there is a small reduction in the $\nu(\text{As=O})$ frequency (880 to 870, or perhaps 845 cm^{-1}), but in (3) the shift (to *ca.* 800 cm^{-1}) is so much greater as to be characteristic of an O_l bridge between a pair of metal centres.[10] This feature would thus account for the composition of (3) as $MoO_3(AsPh_3O)_{0.5}$.

The polymeric compounds (2)—(5) are structurally different from the linear polymer (1a). Whereas (1a) shows four $\nu(\text{Mo-O}_t)$ bands corresponding to the presence of two different *cis*-dioxo-centres [tetrahedral $(O_b)_2Mo(O_t)_2$ and octahedral $(O_b)_2Mo(O_t)_2(dmso)_2$], (2)—(5) all show only one strong band in the $\nu(\text{Mo-O}_t)$ region. Before discussing the structures of these compounds formed through ligand addition to the trioxide, we consider first the simpler case of bridge cleavage through ligand addition to the digol complex $[\{MoO_2(deg)\}_n]$ (7).

Ligand Addition to the Digol Complex (7).—In this compound the tridentate dianion $^-OCH_2CH_2OCH_2CH_2O^-$, is *mer*-co-ordinated and the ' molecular units ' are linked through unsymmetrical core bridges to form a linear polymer.[3] The compound reacts with dmso and py to form adducts $[MoO_2(deg)(dmso)]$ (8) and $[MoO_2(deg)(py)]$ (9). In neither case is there modification of the deg co-ordination because the C–O and Mo-O_l frequencies are almost unchanged. But in both compounds the broad band at 847 cm^{-1} to be attributed to the O_{tb} bridging in (7) is absent (see Figure 2), leaving two closely spaced bands [920, 910 in (8); 915, 905 cm^{-1} in (9)]

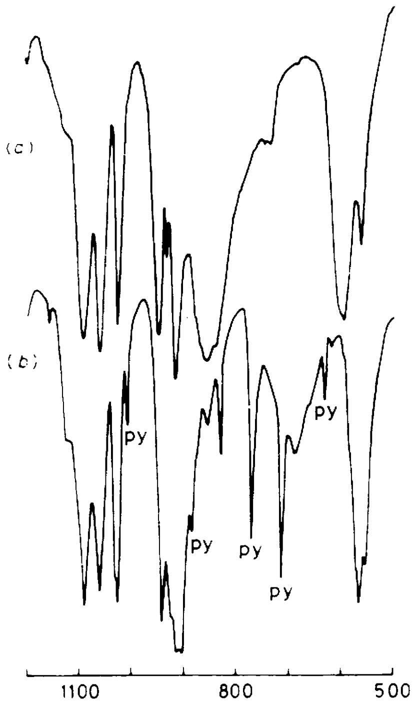
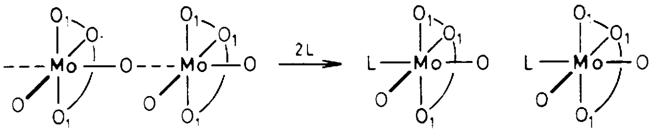


Figure 2. Infrared spectra of (*a*) [$\{MoO_2(deg)\}_n$], showing the broad band at 847 cm^{-1}, and (*b*) the pyridine adduct [$MoO_2(deg)(py)$] (9)

which indicate reversion to a *cis*-dioxo-core. The compounds are therefore considered to arise through bridge cleavage by the ligand L, as shown in Scheme 2.



Scheme 2.

Structures of the Complexes (2)—(5).—The presence of only one ν(Mo–O$_t$) band in conjunction with the low ligand : molybdenum ratio point to structures more highly polymerised than that of (1a). The *X*-ray diffractograms of the compounds all show a strong low-angle reflection corresponding to a *d*-value greater than the inter-layer spacing for molybdenum trioxide itself (d_{020} = 6.93 Å).[11,12] This suggests layered structures with the ligands co-ordinated on one side, or on both sides of planes of molybdenum atoms.

Of the i.r. bands shown by the molybdic acids, which can be taken as hydrate complexes of known structure, the ν(Mo–O$_t$) frequencies could be affected by H-bonding and other features, but the Mo–O–Mo bridging frequencies should reflect broad relationships. The bridging bands shown by (2)—(5) relate to the yellow acid, but not to the white acid, whose bridging band lies at lower frequency (Figure 3). The molybdenum co-ordination environment is therefore as in Figure 4, but the evidence does not show whether there is an alternation in the O$_t$ and L positions, as in the yellow acid.

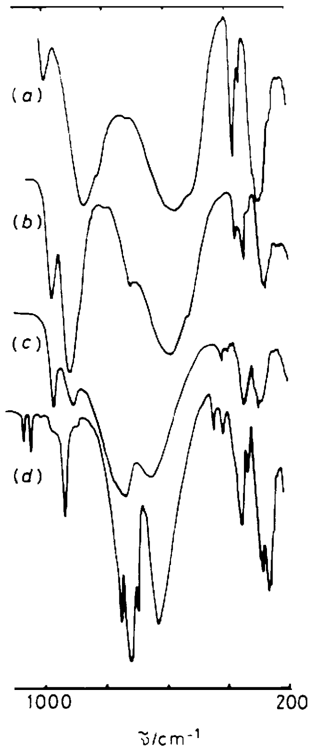


Figure 3. Infrared spectra of (*a*) molybdenum trioxide, (*b*) white molybdic acid [$\{MoO_3(OH_2)\}_n$], (*c*) yellow molybdic acid, [$\{MoO_3(OH_2)\}_n$]·nH$_2$O, and (*d*) the pyridine complex [$\{MoO_3(py)\}_n$] (4). The similarity of the bridging bands at 600—500 cm^{-1} in (*a*) and (*b*), and at 740—630 cm^{-1} in (*c*) and (*d*), is apparent

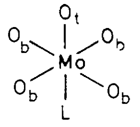


Figure 4. Molybdenum co-ordination proposed for the polymeric complexes (2)—(5)

The structural similarity with *yellow* molybdic acid means that the transformation of molybdenum trioxide to the polymeric complexes involves a structural rearrangement beyond the cleavage of the asymmetric bridges of the trioxide, for this bridge cleavage alone would give derivatives having the type of molybdenum–oxygen structure found in the white acid. Reaction routes leading to (2) and (3) show that their particular core structures can arise not only from this rearrangement, but also from a polymerisation, as in their formation from [$MoO_2(acac)_2$] (Scheme 1). Moreover, the formation of (4) from (1a) clearly involves a rearrangement of the polymeric molybdenum–oxygen framework.

The similarity of the i.r. spectrum of the white acid to that of the trioxide [13,14] is evident from Figure 3. It can be suggested that the low frequencies (Table 1) of the broad Mo–O–Mo bands of these two compounds arise from the presence of the longer Mo–O bonds to the triply bridging oxygen atoms in their structures.[1,2,6] Triple bridging is not present in yellow molybdic acid,[7] nor presumably therefore in compounds (2)—(5).

Behaviour of Molybdenum Trioxide towards Pyridine.—There is evidence that the reactivity of crystalline molybdenum trioxide towards pyridine, and even the course of the reaction, are dependent upon the condition of a particular oxide sample. Bernard and Camelot,[15] who found that in boiling

Table 2. Products from condensation reactions using triethoxymethane

Reactants	Solvent	Product [a]
(1a) with H_2amp	dmso	$[MoO_2(amp)(dmso)]$ (10)
(1a) with H_2amp	ethanol	$[(MoO_2)_2(amp)(Hamp)_2]$ [b] (11)
(1a), H_3hmmp, ethanol	ethanol	$[MoO(hmmp)(OEt)]$ [c] (12a)
$[MoO_2(Hhmmp)]$,[d] ethanol	ethanol	$[MoO(hmmp)(OEt)]$ [c] (12b)

[a] Formulations are based on analyses and i.r. spectra. [b] This compound is also obtainable directly from molybdenum trioxide, and from $[MoO_2(acac)_2]$ through ligand exchange. [c] (12a) and (12b) are isomers. [d] Ref. 9.

Table 3. *X*-Ray *d* values for molybdenum trioxide derivatives [a]

MoO_3 [b]	6.93vs, 3.81s, 3.47vs, 3.25w, 3.01w, 2.61w, 2.30vs, 2.27m, 1.96w, 1.70m, 1.60w, 1.57m
$[\{MoO_3(OH_2)\}_n]$	9.08s, 5.28w, 4.56m, 3.45vs, 3.04m, 2.53m, 2.10m, 1.99m, 1.95w, 1.86w, 1.64m
$[\{MoO_3(OH_2)\}_n]\cdot nH_2O$	6.86s, 3.77m, 3.65m, 3.45ms, 3.30m, 3.23w, 2.64w, 2.31m, 1.96w, 1.95w, 1.89w, 1.83w, 1.73w
(1a) $[\{MoO_3(dmso)_{1.33}\}_n]$	7.70m, 7.37vs, 7.19m, 7.03m, 6.86m, 4.29m, 4.21m, 4.11m, 3.87m, 3.77m, 3.63m, 3.44m, 2.85m, 2.82m, 2.75m, 2.39w, 2.17w
(1b) $[\{MoO_3(dmso)_{1.33}\}_n]$	8.27w, 6.73vs, 4.60w, 3.92ms, 3.66ms, 3.36s, 3.18m, 3.06m, 2.98m, 2.88m, 2.75w, 2.66w, 2.56m, 2.49w, 1.68w
(2) $[\{MoO_3(pyo)\}_n]$ [c]	9.51m, 8.27s, 8.04s, 6.07w, 4.87w, 4.39w, 3.72m, 3.62w
(3) $[\{MoO_3(AsPh_3O)_{0.5}\}_n]$	12.27m, 8.75vs, 7.14w, 6.19w, 5.54m, 5.10m, 4.21w, 4.15m, 2.86w
(4) $[\{MoO_3(py)\}_n]$	11.48vs, 5.72s, 3.88m, 3.10m, 2.85m, 2.52m, 2.01w, 1.92w, 1.79w, 1.54w
(5) $[\{MoO_3(AsPh_3O)\}_n]$	11.95s, 10.65m, 9.02ms, 7.69m, 7.14w, 6.61m, 4.51m, 4.13w, 3.58w

[a] Weakest reflections are omitted. [b] Thermally recrystallised sample. [c] Samples gave blunted peaks due to poor crystallinity.

pyridine at 115 °C molybdenum trioxide shows only a superficial reaction, used a sealed tube at 160—170 °C for 30 d to obtain a product, $[MoO_3(py)]$. Tominaga *et al.*[12] reported a progressive uptake of pyridine over several days at 115 °C. They interpreted their results in terms of formation of an intercalation phase with the pyridine molecules lying between the non-bonded layers of the molybdenum trioxide lattice, although this was based on an assumption 'that the pyridine enters the crystal layers bonded by van der Waals forces, and that the only face spaces to increase are those perpendicular to the *b* axis, with no changes occurring in the grid constants of the other axes.'

In the present work, sealed-tube experiments failed to yield the complex. With pure dry pyridine, blackening of the trioxide through reduction set in at 120—140 °C. The effect spread from initial points of attack, as though self-propagating. Presence of moisture inhibited this reaction, but gave a pyridinium salt. Our samples of (4), from the trioxide, were obtained under pyridine reflux after 21—28 d. The conversion of (1a) into (4) is more rapid, and with availability of (1a) this offers a more acceptable preparative route. The i.r. spectrum of (4) matched that of Camelot,[14] but the evidence from the *X*-ray diffractograms was not fully compatible with Tominaga's [12] results. It would seem that in his experiments the strong 020 line disappeared when the pyridine uptake corresponded to $MoO_3(py)_{0.2}$, but for our samples this reflection disappeared only as the product approached the limiting composition $MoO_3(py)$. We class our product as a polymeric complex rather than an intercalation phase, although its formation may be through an intercalation step. Johnson *et al.*[16] have recently reached the same conclusion on $MoO_3(py)$ by showing that *X*-ray powder data can be refined to a tetragonal unit cell, where dimensions are consistent with a structure similar to that of yellow molybdic acid. As the trioxide reacted with pyridine, its i.r. spectrum gave way to an entirely different spectrum containing new $\nu(Mo-O_t)$ and Mo–O–Mo bridging vibrations (Figure 3). There is displacement of the pyridine band at 403 cm^{-1} to higher frequency (420, 450 cm^{-1} with splitting) as is characteristic of co-ordination,[17] but identification of the ν(Mo–py) vibration is uncertain. Having regard to the stability of the complex, Camelot [14] suggested that ν(Mo–py) may be so high as to fall within the composite band at 640—630 cm^{-1}. The only possible lower frequencies are 355 and 280 cm^{-1}. However, these frequencies are common to all four spectra in Figure 2, and the former is probably to be assigned to $\delta(Mo-O_t)$. It could be argued that the band at 280 cm^{-1} shows some enhancement and resolution as compared with the molybdic acid spectra, and that it falls within the range of ν(M–py) values established by Clark and Williams [17] for many pyridine-metal halide compounds (with oxidation states + 2 and + 3). Wherever it lies, the ν(Mo–py) absorption must be weak, as through low bond polarity.

Products from Condensation Reactions of $[\{MoO_3(dmso)_{1.33}\}_n]$ (1a).—This derivative provides a reactant of effective core stoicheiometry MoO_3, which is soluble in dmso or alcohols. Besides entering into ligand-exchange reactions it can be condensed with hydroxylic compounds under mild conditions through the use of triethoxymethane (teom). New products from its reactions with 2-amino-2-methylpropane-1,3-diol (H_2amp) and 2-hydroxymethyl-2-methylpropane-1,3-diol (H_3hmmp) are listed in Table 2.

Of the two products (10) and (11) from the reaction of (1a) with H_2amp, (10) is formed when the dmso concentration in the solution is high. Besides showing a compositional analogy to the complex $[\{MoO_2(npg)(OH_2)\}_2]$ [9,18] from 2,2-dimethylpropane-1,3-diol (neopentyl glycol, H_2npg), (10) gives a strong ligand-bridging band at almost the same frequency (635 *vs.* 642 cm^{-1}). A similar dimeric constitution, with one end of the 1,3-diolato-chelating chain bridging a pair of molybdenum centres, is therefore inferred. The structure of (11) is speculative, but on the basis of probable alkoxy bridging by amp (i.r. spectrum) there is again a formal compositional analogy with a compound of known structure,[19] *viz.* *cis*-di-μ-methoxo-bis{[2,3-dimethylbutane-2,3-diolato-(1 –)]dioxomolybdenum(VI)}-methanol (1/2).

The formation of the two yellow isomeric hmmp derivatives

(12a) and (12b) arises from the use of different reactants. Differences in their C–O and Mo–O_b vibrations suggest a difference in the O_t bridging. Through promoting a higher degree of condensation with the ligand, the use of teom leads to the formation of an MoO core, and the compounds thus stand apart from an MoO_2 class of hmmp–alkoxy compounds of composition $(MoO_2)_2$(hmmp)(OR), which forms in the absence of the condensing agent. The ethoxy member (13) of this latter series has been shown to have the dimeric formulation [{$(MoO_2)_2$(hmmp)(OEt)}$_2$],[20] with the hmmp oxygen atoms giving a system of double and triple bridges of the kind known in [{Ti(OEt)$_4$}$_4$] and [{W(OEt)$_4$}$_4$].[21]

Experimental

Reactants and solvents were dried by standard methods. Pyridine, dried over barium oxide, was fractionally distilled to a 0.2 °C boiling range.

For most purposes AnalaR molybdenum trioxide was used directly, after drying at *ca.* 200 °C. Recrystallised oxide was obtained by heating to 620 °C for 4 d in dry air.[12] The yellow and white molybdic acids were prepared according to Brauer,[22] the white acid being obtained *without* seeding. A sample of the white acid, dried at 100 °C, at which temperature the phase $MoO_3 \cdot H_2O$ is reported to be stable,[23] gave Mo, 59.5% (calc. 59.3%).

Tubes required for sealing were prepared by use of a high-vacuum line. Products were washed with unreactive solvents, usually ethanol or benzene, diethyl ether, and light petroleum (b.p. 50–70 °C) in succession, with final drying in moisture-free air. *X*-Ray diffractograms (Table 3) were used for identification of crystalline phases, and the slow reactions of molybdenum trioxide with py, pyo, and $AsPh_3O$ were best followed from the diffractograms. Analyses are given in Table 4.

[{MoO_3(dmso)$_{1.33}$}$_n$] (1a).—To obtain concentrated solutions, MoO_3 (13 g) was stirred in dmso (50 cm^3) for up to 20 h at 120—130 °C. Crystallisation is sensitive to nucleation and diffusion effects. At room temperature onset of crystallisation is very slow with micro-nodules of (1) appearing only after *ca.* 2 weeks, but with stirring crystallisation was complete after 4—5 d. Above 70—80 °C, and especially with 10—15% water in the solution, well developed plates (sub-circular or parallelepiped) or nodular clusters of plates form within 24 h, although the solution is still prone to supersaturation. The identity of these crystals with the crystal whose structure has been reported was confirmed by determination of cell parameters [Found (20 °C): a = 15.627(3), b = 19.316(4), c = 8.474(2) Å, α = 100.62(2), β = 90.78(2), γ = 112.22(2)°. Reported[8] (−100 °C): a = 15.563(3), b = 19.224(3), c = 8.391(1) Å, α = 100.85(1), β = 90.94(1), γ = 112.36(1)°]. Analytical compositions of crystals obtained at 80—100 °C averaged MoO_3(dmso)$_{1.35}$, close to the crystallographic requirement, MoO_3(dmso)$_{1.33}$, but samples formed at room temperature were of typical composition MoO_3(dmso)$_{1.40}$. There was no decisive modification of the diffraction patterns given by samples obtained at the lower temperatures, and the cause of the small compositional difference has not been established. Slow crystallisation from solution at 100—120 °C gave needle-like crystals of a second phase (1b) of the same composition as the plates, and often in admixture with them. (1a) and (1b) are stable in air and begin to lose dmso only at 100 °C under high vacuum.

We did not encounter other crystalline phases, as reported by McCarron and Harlow.[8] The crystallisation behaviour of solutions obtained from white molybdic acid (at 120 °C) or the yellow acid (at room temperature) was similar to that of solutions of the trioxide.

Table 4. Elemental analyses (%), with calculated values in parentheses

Compound	C	H
(1a) [MoO_3(dmso)$_{1.33}$] [a]	13.1 (12.9)	3.3 (3.2)
(1b) [MoO_3(dmso)$_{1.33}$] [b]	13.0 (12.9)	3.5 (3.2)
(2) [MoO_3(pyo)]	25.1 (25.1)	2.35 (2.1)
(3) [MoO_3($AsPh_3O$)$_{0.5}$]	35.6 (35.35)	2.7 (2.45)
(4) [MoO_3(py)] [c]	27.1 (26.9)	2.4 (2.2)
(5) [MoO_3($AsPh_3O$)$_{0.92}$] [d]	45.1 (45.0)	3.7 (3.2)
(6) [Mo_2O_5(acac)$_2$(dmso)$_2$]	27.2 (26.8)	4.4 (4.15)
(8) [MoO_2(deg)(dmso)]	22.7 (22.3)	4.5 (4.5)
(10) [MoO_2(amp)(dmso)] [e]	23.3 (23.3)	4.8 (4.85)
(11) [$(MoO_2)_2$(amp)(Hamp)$_2$] [f]	25.1 (25.4)	5.6 (5.1)
(12a) [MoO(hmmp)(OEt)] [g]	31.0 (30.7)	5.1 (5.1)
(12b) [MoO(hmmp)(OEt)] [h]	30.7 (30.7)	5.25 (5.1)
(13) [{$(MoO_2)_2$(hmmp)(OEt)}$_2$]	20.6 (20.1)	3.6 (3.35)
(14) [{$(MoO_2)_2$(hmmp)(OPr^i)}$_2$]	21.8 (22.2)	4.3 (4.3)
(15) [{$(MoO_2)_2$(hmmp)(OBu^t)}$_2$]	24.5 (24.2)	4.5 (4.0)
(16) [{$(MoO_2)_2$(hmmp)(OMe)}$_2$]·2MeOH	20.8 (20.5)	3.8 (4.2)

[a] Mo, 38.3 (38.7); S, 17.3 (17.2%). [b] Hand-sorted needles. Mo, 38.2 (38.7%). [c] Product from reaction of pyridine with (1a). Mo, 43.1 (43.0%). [d] Mo, 22.1 (21.8%). [e] N, 4.5 (4.4); S, 10.0 (10.4%). [f] N, 7.1 (7.4%). [g] Mo, 34.7 (35.0%). [h] Mo, 34.6 (35.0%).

[{MoO_3(pyo)}$_n$] (2).—MoO_3 (1.0 g) was stirred with pyo (5.0 g) in chlorobenzene (50 cm^3) at 125—130 °C for 12 h. The reaction of pyo with white molybdic acid occurred under similar conditions.

[{MoO_3($AsPh_3O$)$_{0.5}$}$_n$] (3).—MoO_3 (1.0 g) was stirred with the ligand (5.5 g) in bromobenzene (50 cm^3) for 15 h under reflux. Further uptake of ligand beyond the 0.5 : 1 ratio to give (5) was very slow. After 75 h the ratio had risen to 0.57 : 1.

[{MoO_3(py)}$_n$] (4).—MoO_3 (2 g), recrystallised and ground, was stirred under boiling py (80 cm^3) with a slow stream of dry air to exclude moisture. After 6 d the composition of the bulky yellow product was MoO_3(py)$_{0.45}$, after 13 d MoO_3(py)$_{0.74}$, and after 27 d MoO_3(py)$_{0.97}$. Using (1a) as reactant, 1.0 g was stirred under reflux in py (40 cm^3). A white intermediate formed during the first 2 h before transformation to (4) began. Heating was continued for 15 h. Analysis gave the composition MoO_3(py)$_{1.00}$. The compound is stable in air and loses pyridine only at 180—200 °C under high vacuum.

[{MoO_3($AsPh_3O$)}$_n$] (5).—[MoO_2(acac)$_2$] (1.0 g) and $AsPh_3O$ (1.0 g) dissolved in benzene (40 cm^3) gave an immediate white precipitate, but to complete the reaction the mixture was heated for 5 min in an open flask. The white solid separated from the clear solution.

$[\mathrm{Mo_2O_5(acac)_2(dmso)_2}]$ (6).—$[\mathrm{MoO_2(acac)_2}]$ (0.63 g) was dissolved in ethanol (6 $\mathrm{cm^3}$) and dmso (4 $\mathrm{cm^3}$). The solution was heated to 40 °C for 10 min. White crystals separated over 2–3 d. The i.r. spectrum showed a strong band at 770 $\mathrm{cm^{-1}}$ characteristic of an Mo–O–Mo bridge, together with features characteristic of co-ordinated acetylacetonate and dmso.

$[\mathrm{MoO_2(deg)(dmso)}]$ (8).—$[\mathrm{MoO_2(deg)}]$[9] (0.4 g) was dissolved in dmso (1.2 $\mathrm{cm^3}$) and teom (6 $\mathrm{cm^3}$) added before heating the solution to boiling. Blue-white crystals of (8) separated on cooling. The pyridine analogue (9) was obtained by quantitative absorption of pyridine from the saturated vapour at room temperature.

$[\mathrm{MoO_2(amp)(dmso)}]$ (10).—Dimethyl sulphoxide solutions containing the ligand (2 g in 4 $\mathrm{cm^3}$) and $\mathrm{MoO_3}$ (1.6 g in 8 $\mathrm{cm^3}$) were mixed; teom (7 $\mathrm{cm^3}$) was added and the solution heated to 80 °C. Crystals of the product separated overnight. The spectrum showed a band at 640 $\mathrm{cm^{-1}}$, consistent with bridging by ligand oxygen.[7]

$[\mathrm{(MoO_2)_2(amp)(Hamp)_2}]$ (11).—Solutions containing (1a) (2.2 g in 30 $\mathrm{cm^3}$ ethanol and 3 $\mathrm{cm^3}$ teom) and the ligand (2.0 g in 8 $\mathrm{cm^3}$ ethanol and 18 $\mathrm{cm^3}$ teom) were mixed and brought to boiling. Crystals of (11) formed on standing. There was also a further product, of probable composition $\mathrm{MoO_2(amp)}$, but it was not obtained pure.

Alternative preparation of (11) *from molybdenum trioxide.* The oxide (1 g) was stirred at 120—130 °C with the molten ligand (10 g) until reaction was complete (*ca.* 1 h). The mixture was allowed to solidify and the excess ligand extracted in dry ethanol.

$[\mathrm{MoO(hmmp)(OEt)}]$ (12a).—This isomer was produced through reaction of $\mathrm{H_3hmmp}$ (0.55 g) with (1a) in ethanol (10 $\mathrm{cm^3}$) and teom (6 $\mathrm{cm^3}$). The solution became yellow when brought to boiling and the finely crystalline product quickly separated.

$[\mathrm{MoO(hmmp)(OEt)}]$ (12b).—A suspension of $[\mathrm{MoO_2(Hhmmp)}]$ (0.5 g) in ethanol (100 $\mathrm{cm^3}$) and teom (9 $\mathrm{cm^3}$) slowly dissolved under reflux, over 2—3 h. The product separated as a yellow crystalline powder during the later stages. It is a possibility that in the preparations of (12a) and (12b) there is a small mutual contamination, since weak i.r. bands in the one compound correspond to strong bands in the other.

$[\{\mathrm{(MoO_2)_2(hmmp)(OR)_2}\}_2]$[R = Et (13), $\mathrm{Pr^i}$ (14), *or* $\mathrm{Bu^i}$ (15)].—$[\mathrm{MoO_2(Hhmmp)}]$ (*ca.* 1 g) on the fritted filter of an extraction unit was slowly leached (12—20 h) into the boiling alcohol, ROH (*ca.* 60 $\mathrm{cm^3}$). With each of the alcohols (EtOH, $\mathrm{Pr^iOH}$, and $\mathrm{Bu^iOH}$), the finely crystalline product separated as the extraction proceeded. A small flow of dry air through the extractor prevented access of moisture. The methanolate (16), of composition $\mathrm{(MoO_2)_2(hmmp)(OMe)\cdot MeOH}$, was obtained in a sealed tube over 7 d at 60—80 °C. The i.r. spectra of the compounds pointed to closely related core structures. Derivatives (14), (15), and (16) are therefore considered to be of the same structural type as (13).

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