# Novel Methanol-Containing Oxomolybdate(v) Complexes: Synthesis and Structural Characterisation of Intermediates in the Formation of $\{Mo_2O_4\}^{2+}$ Clusters from $[MoOCl_4(H_2O)]^-$ and $[MoOBr_4]^-$ Precursors

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A series of oxomolybdate(v) complexes with methanol was prepared by the reaction of $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ (**1**) or $(PyH)[MoOBr_4]$ ($PyH^+$ = pyridinium cation, $C_5H_5NH^+$) in methanol. $(PyH)_2[MoOCl_4(MeOH)]Cl$ (**2**) is obtained upon substitution of coordinated water for methanol in **1**. Small amounts of weak bases such as pyridine or trifluoroacetate promote further substitution chemistry at the labile sites, followed by dimerisation to the well-known $\{Mo_2O_4\}^{2+}$ core. A dinuclear anion with coordinated methanol can be isolated as its pyridinium salt, $(PyH)_2[Mo_2O_4Cl_4(MeOH)_2]$, in two crystalline modifications, either as a triclinic (**3**) or as an orthorhombic polymorph (**4**). After prolonged reaction times further assembly of dinuclear fragments takes place and tetranuclear $[Mo_4O_8(OMe)_2(MeOH)_2Cl_4]^{2-}$ is formed. The products of the analogous reactions with $(PyH)[MoOBr_4]$ as the starting material depend largely upon the reaction temperature. Dinuclear $(PyH)_2[Mo_2O_4Br_4(MeOH)_2]$ (**5**), which crystallises in an orthorhombic unit cell and whose structure is isotypic to that of **4**, is obtained only if the reaction takes place at low temperature (5 °C); under ambient conditions $(PyH)_2[Mo_4O_8(OMe)_2(MeOH)_2Br_4]$ (**6**) is obtained instead. The tetranuclear anion of **6** consists of a commonly adopted assembly of two $\{Mo_2O_4\}^{2+}$ units. The identity of the products was determined by infrared spectroscopy and X-ray structure analyses.


## Introduction

$\{Mo_2O_4\}^{2+}$ clusters with metal d electrons localised in single metal–metal bonds occupy a prominent position among the polyoxometallates, which continue to be a subject of great interest because of their potential applications ranging from catalysis to medicine.[1] Their basic building blocks, dinuclear $\{Mo_2O_4\}^{2+}$ moieties (Scheme 1) with a well-defined geometry,[2,3] can assemble in many different ways and lead to a variety of metal oxide cores, as illustrated by some recently prepared clusters, i.e., $[(Mo_2O_4)_4(OMe)_6(MeOH)_4Cl_2]$,[4] bimetallic alkoxides $[M_2(Mo_2O_4)_2(O\mathit{i}Pr)_{14}]$ (M = Ta, Nb),[5] $[(Mo_2O_4)_6(\mu_2\text{-}SO_3)_{12}(\mu_3\text{-}SO_3)_4]^{20-}$,[6] $[Na_4(H_2O)_6\{(Mo_2O_4)_{10}(P_2O_7)_{10}(CH_3COO)_8(H_2O)_4\}]^{24-}$,[7] $[(Mo_2O_4)_3(O_3PCH_2PO_3)_3(MoO_4)]^{8-}$,[8] $[Na(H_2O)_2\{(Mo_2O_4)_4(O_3PCH_2PO_3)_4(CO_3)_2\}]^{11-}$,[9] and a series of nano-sized, mixed-valence $Mo^V/Mo^{VI}$ acetate complexes.[10] Theoretical calculations have been performed on some of these species in order to understand the bonding of such complex architectures.[11] Although the $\{Mo_2O_4\}^{2+}$ species were considered at first to be essentially products of inadvertent air oxidation, contemporary research in this field is aimed towards the development of more rational and high-yield synthetic procedures.

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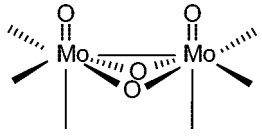


Scheme 1. A basic building unit: $\{Mo_2O_4\}^{2+}$ structural fragment.

We have demonstrated in our previous work that $(PyH)_2[MoOCl_5]$ reacts almost instantaneously in mixtures of methanol and pyridine to form discrete clusters built of two, three, four or six $\{Mo_2O_4\}^{2+}$ subunits.[12] A simple, high-yield preparation method, coupled with the relative stability and the fact that the coordinated chlorides are labile enough under appropriate conditions to allow a facile substitution chemistry, have made $(PyH)_2[MoOCl_5]$ an attractive starting material. Since the widely accepted notion, based on the analytical and spectroscopic data, was that its structure consists of octahedral $[MoOCl_5]^{2-}$ ions,[13] its X-ray structure analysis has not been undertaken until now. The general reaction route leading to $\{Mo_2O_4\}^{2+}$ clusters was proposed to begin with rapid substitution of the chlorides, followed by dimerisation through $Mo(\mu_2\text{-}O)_2Mo$ bridges with concomitant interaction between the two $d^1$ ions. There are three sites per metal in the $\{Mo_2O_4\}^{2+}$ moiety that are open for coordination of, preferably, oxygen-donor ligands. The multitude of known $\{Mo_2O_4\}^{2+}$ complexes with very diverse mono-, bi- or multidentate ligands suggests that many fulfil the metal's coordination demands.[14]

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In the absence of ligands in sufficient concentrations, the metal centres attain coordination saturation through the self-assembly of $\{Mo_2O_4\}^{2+}$ units by sharing the initially $\mu_2$-bridging oxo groups. The surface of the clusters thus obtained still possesses sites available for coordination, but their number is greatly reduced compared to the $\{Mo_2O_4\}^{2+}$ subunit. A very important aspect in the process is the formation of methoxide ions and their subsequent incorporation into the cluster, which diminishes its negative charge. Because of the ability of alkoxides to participate in bridging interactions with two or three metal centres, the assembly of $\{Mo_2O_4\}^{2+}$ units in their presence results in a different core structure, as exemplified by the association of two $\{Mo_2O_4\}^{2+}$ units to form a tetranuclear core.[15] The alkoxide was shown to assist in the assembly and either a compact $\{Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OR)_2\}^{2+}$ or more rarely $\{Mo_4O_4(\mu_2\text{-}O)_4(\mu_2\text{-}OR)_2\}^{2+}$ core with an open structure were formed. With no alkoxide present, a self-assembly into a cube-like $\{Mo_4O_4(\mu_3\text{-}O)_4\}^{4+}$ core was observed.

The ongoing research in our laboratory has been focused on the isolation and characterisation of the intermediate products in the formation of $\{Mo_2O_4\}^{2+}$ clusters. Knowing their identities would help to elucidate a multi-step reaction pathway from the starting oxohalomolybdate(v) to the final $\{Mo_2O_4\}^{2+}$ clusters. In this context, the reactions of $(PyH)_2[MoOCl_5]$ and $(PyH)[MoOBr_4]$ with pyridine or pyridinium trifluoroacetate in methanol were investigated. Prior to that, however, $(PyH)_2[MoOCl_5]$ was subjected to an X-ray structure analysis.

## Results and Discussion

### Structural Data

#### *Structure of $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ (1)*

The X-ray structure analysis of $(PyH)_2[MoOCl_5]$ revealed its true identity as $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$, whose structure is isotypic with that of $(PyH)_5[MoOBr_4(H_2O)]_3Br_2$.[16] The orthorhombic unit cell contains six $[MoOCl_4(H_2O)]^-$ ions, four non-coordinated chloride ions and ten protonated pyridine molecules as countercations.. There are two crystallographically distinct $[MoOCl_4(H_2O)]^-$ ions (depicted in Figure 1). The one containing Mo(1) lies at the intersection of two mirror planes, with the chloro ligands in the planes and Mo(1), O(11) and O(12) on the twofold axis. Its symmetry is $C_{2v}$. The other anion has only one crystallographically imposed mirror plane. Mo(2), both oxygen atoms and the two chlorine atoms Cl(21) and Cl(23) lie in this plane. The distorted octahedral environments of Mo(1) and Mo(2) reveal the usual bonding pattern for $[MoOCl_4(H_2O)]^-$ anions:[17] (i) a short Mo=O bond [1.648(4) and 1.650(3) Å], consistent with a multiple bond character, (ii) a water ligand at 2.284(4) and 2.270(3) Å in a position *trans* to the terminal oxo group, and (iii) a displacement of molybdenum from the plane of the four chloro ligands towards the oxo group [0.334(1) Å for Mo(1) and 0.349(1) Å for Mo(2)]. An exhaustive list of structural parameters is given in Table 1.

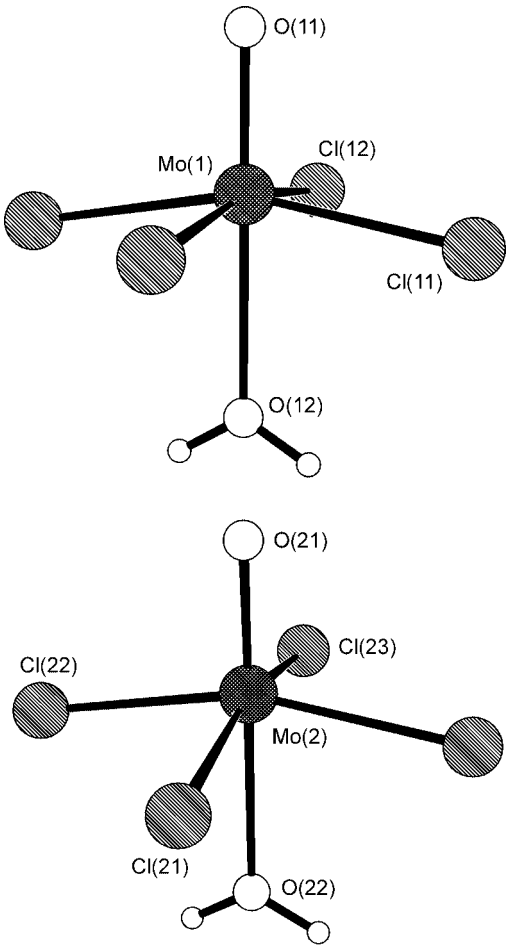



Figure 1. The two crystallographically independent $[MoOCl_4(H_2O)]^-$ ions found in compound **1**. The same drawing scheme pertains to all figures: molybdenum atoms are cross-hatched; chlorine or bromine atoms are lined bottom right to top left; nitrogen atoms are lined bottom left to top right; oxygen atoms are unshaded and carbon atoms shaded, medium-sized spheres and hydrogen atoms are unshaded small-sized spheres.

Table 1. Geometric parameters [Å; °] of the $[MoOCl_4(H_2O)]^-$ ions in **1**.

| | | | |
|---|---|---|---|
| Mo(1)–O(11) | 1.648(4) | Mo(2)–O(21) | 1.650(3) |
| Mo(1)–O(12) | 2.284(4) | Mo(2)–O(22) | 2.270(3) |
| Mo(1)–Cl(11) | 2.3671(9) | Mo(2)–Cl(21) | 2.4065(12) |
| Mo(1)–Cl(12) | 2.3779(12) | Mo(2)–Cl(22) | 2.3698(7) |
| | | Mo(2)–Cl(23) | 2.3535(11) |
| O(11)–Mo(1)–Cl(11) | 99.76(3) | O(21)–Mo(2)–Cl(21) | 95.66(14) |
| O(11)–Mo(1)–Cl(12) | 96.45(4) | O(21)–Mo(2)–Cl(22) | 176.96(16) |
| O(11)–Mo(1)–O(12) | 180.0 | O(21)–Mo(2)–Cl(23) | 99.56(14) |
| Cl(11)–Mo(1)–Cl(12) | 88.909(8) | O(21)–Mo(2)–O(22) | 176.96(16) |
| Cl(11)–Mo(1)–Cl(11)[a] | 160.49(6) | Cl(21)–Mo(2)–Cl(22) | 89.07(2) |
| Cl(12)–Mo(1)–Cl(12)[a] | 167.10(8) | Cl(22)–Mo(2)–Cl(23) | 88.48(2) |
| Cl(11)–Mo(1)–O(12) | 80.24(3) | Cl(21)–Mo(2)–Cl(23) | 164.77(5) |
| Cl(12)–Mo(1)–O(12) | 83.55(4) | Cl(22)–Mo(2)–Cl(22)[b] | 161.40(4) |
| | | Cl(21)–Mo(2)–O(22) | 81.29(10) |
| | | Cl(22)–Mo(2)–O(22) | 80.71(2) |
| | | Cl(23)–Mo(2)–O(22) | 83.48(10) |

[a] Symmetry code: $-x + 1/2, 2 - y, z$. [b] Symmetry code: $x, 2 - y, z$.

A complicated pattern of hydrogen bonds is formed in **1**. Six hydrogen bonds link three $[MoOCl_4(H_2O)]^-$ ions through water ligands to a pair of non-coordinated chloride ions (Figure 2a). Each water molecule is engaged in two

hydrogen bonds with two chlorides, with lengths of 3.164(3) and 3.129(2) Å. Three pyridinium cations are connected in a similar manner by bifurcated, rather long, hydrogen bonds with a pair of chloride counterions [N(1)···Cl = 3.3299(30) and N(2)···Cl = 3.3876(44) Å; Figure 2b]. Alternation of both types of trimeric assemblies through common chloride ions produces infinite chains which are parallel to the *b* axis (Figure 2c). The environment of each chloride ion in the chain is that of a distorted octahedron consisting of three water molecules and three pyridinium nitrogens.

The $[MoOCl_4(H_2O)]^-$ ion has been structurally characterised in several other compounds.[17] Due to the widespread participation of coordinated water molecules in O–H···Cl or O–H···O(terminal oxo group) hydrogen bonds, pairs of anions or infinite chains are observed in many solid-state structures. The water ligand is bonded in some $[MoOCl_4(H_2O)]^-$ compounds at longer distances. For in-

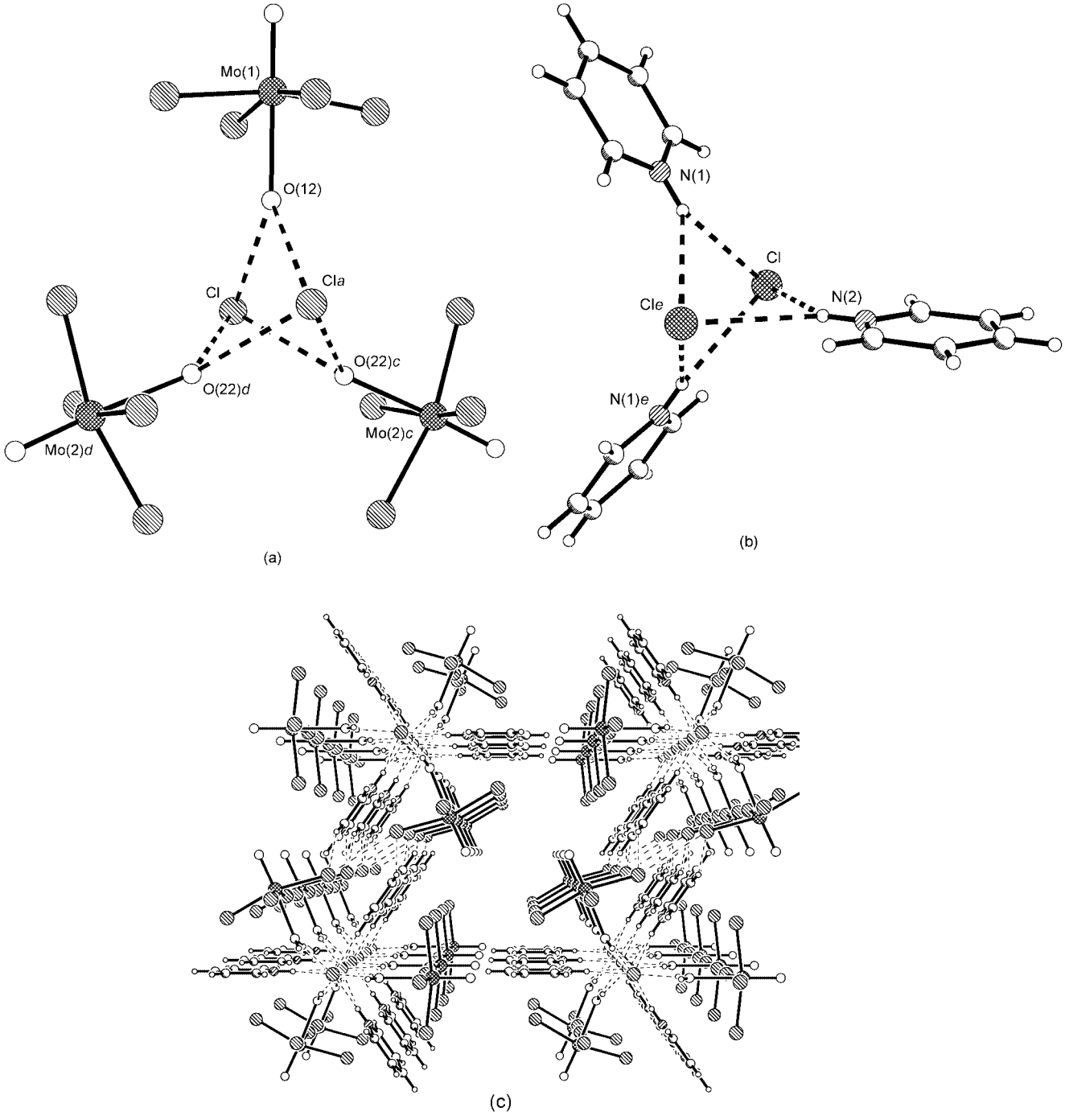



Figure 2. Hydrogen bonds in **1**: (a) three $[MoOCl_4(H_2O)]^-$ ions are linked by a pair of chloride counterions; (b) two chloride ions also link three pyridinium cations. Labels *a*, *c*, *d* and *e* denote symmetry-generated atoms; (c) chains viewed along the *b* axis.

stance, a distance of 2.393(15) Å is observed in $[As(C_6H_5)_4][MoOCl_4(H_2O)]$.[17c] This lengthening is in agreement with the uniform tendency of Mo=O bonds to weaken bonds *trans* to themselves. Nevertheless, the bond lengths in **1** are still significantly longer than related bonds which are not subject to a *trans* influence, for example 2.148(6) Å determined for $[Mo_4O_8(OH)_2(H_2O)_2(C_4O_4)_2]^{2-}$.[18]

### *Structure of (PyH)$_2$[MoOCl$_4$(MeOH)]Cl (2)*

The asymmetric unit of **2** contains a complex anion with the composition $[MoOCl_4(MeOH)]^-$, as shown in Figure 3, a chloride ion and two protonated pyridine molecules as countercations. The $[MoOCl_4(MeOH)]^-$ ions have pseudo-octahedral coordination spheres characterised by a short Mo=O bond, a methanol ligand in a position *trans* to it and four chloro ligands at 2.3715(6)–2.3817(6) Å. The molybdenum atom is, as expected, displaced away from the least-squares plane of the four chlorine atoms by 0.3212(4) Å towards the oxo group. This necessitates obtuse O=Mo–Cl angles in the range 96.80(6)–98.62(6)°. The molybdenum-to-methanol oxygen bond length is 2.2911(15) Å. Relevant structural parameters of the $[MoOCl_4(MeOH)]^-$ ion are summarised in Table 2. The methanol ligand is also engaged in a relatively short hydrogen-bonding interaction with a chloride counterion Cl(5) [O(2)···Cl(5) = 3.0235(16) Å]. The non-coordinated chloride Cl(5) participates in two more hydrogen bonds. Both are formed with pyridinium nitrogen atoms, the distance to N(1)a is 3.0508(21) Å [(*a*) *x*, *y*, 1 + *z*] and the distance to N(2)b is 3.1384(20) Å [(*b*) –0.5 + *x*, 0.5 – *y*, 0.5 + *z*].

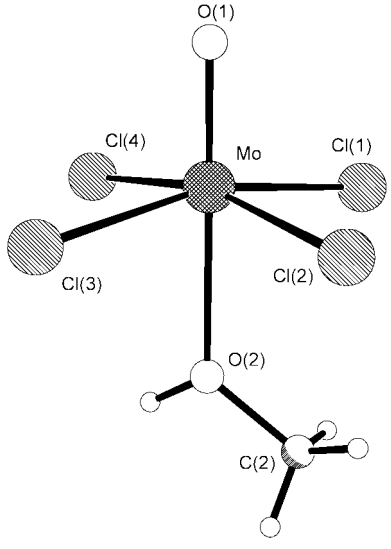



Figure 3. A drawing of the $[MoOCl_4(MeOH)]^-$ unit in **2** with the atom labelling scheme.

Although many $[MoOCl_4L]^-$ compounds with bases, L, such as tetrahydrofuran, dimethylphosphite, dimethylformamide and acetonitrile have been structurally characterised,[19] there were none where L is an alcohol until now. Nevertheless, the existence of the $[MoOCl_4(MeOH)]^-$ ion has been suggested previously in order to explain adequately the electronic spectrum of a methanol solution of $[N(C_4H_9)_4][MoOCl_4]$.[20]

Table 2. Geometric parameters [Å; °] of $[MoOCl_4(MeOH)]^-$ ion in **2**.

| | | | |
|---|---|---|---|
| Mo–O(1) | 1.6581(16) | Mo–Cl(4) | 2.3715(6) |
| Mo–Cl(1) | 2.3750(6) | Mo–O(2) | 2.2911(15) |
| Mo–Cl(2) | 2.3787(5) | O(2)–C(2) | 1.436(3) |
| Mo–Cl(3) | 2.3817(6) | | |
| O(1)–Mo–Cl(1) | 97.38(1) | Cl(4)–Mo–Cl(1) | 90.22(3) |
| O(1)–Mo–Cl(2) | 98.29(6) | Cl(1)–Mo–Cl(3) | 163.98(2) |
| O(1)–Mo–Cl(3) | 98.62(6) | Cl(2)–Mo–Cl(4) | 164.91(2) |
| O(1)–Mo–Cl(4) | 96.80(6) | Cl(1)–Mo–O(2) | 82.83(5) |
| O(1)–Mo–O(2) | 179.78(8) | Cl(2)–Mo–O(2) | 81.80(4) |
| Cl(1)–Mo–Cl(2) | 88.05(2) | Cl(3)–Mo–O(2) | 81.17(4) |
| Cl(2)–Mo–Cl(3) | 88.80(2) | Cl(4)–Mo–O(2) | 83.11(4) |
| Cl(3)–Mo–Cl(4) | 88.74(2) | | |

### *Structure of the Triclinic Modification of (PyH)$_2$[Mo$_2$O$_4$Cl$_4$(MeOH)$_2$] (3)*

A perspective view of the $[Mo_2O_4Cl_4(MeOH)_2]^{2-}$ anion is presented in Figure 4, which also shows the atom labelling scheme used. Each anion occupies a general position within the unit cell of a triclinic space group $P\bar{1}$. Associated with each dinuclear anion are two protonated pyridine molecules. A central $\{Mo_2O_4\}^{2+}$ structural core may be recognized with typical geometric parameters.[3] There are two pairs of terminal and bridging oxo ligands with Mo=O and Mo–O($\mu_2$) distances in the ranges 1.674(4)–1.679(4) and 1.938(8)–1.949(4) Å, respectively. The terminal oxo groups are bent away from each other. The Mo–Mo bond length of 2.5902(6) Å corresponds to a single metal–metal bond. The Mo($\mu_2$-O)$_2$Mo ring is not planar, but is folded by 146.01(10)° around the vector connecting the bridging oxygen atoms. The puckering of the Mo($\mu_2$-O)$_2$Mo ring is presumably a means of allowing a close approach of the metal atoms. A pair of chloro ligands and a methanol *trans* to the terminal oxo group complete a distorted octahedral geometry about each metal atom. The molybdenum-to-methanol oxygen bond lengths are, as expected for bonds in this position, relatively long [2.351(4) and 2.372(4) Å]. Pairs of coor-

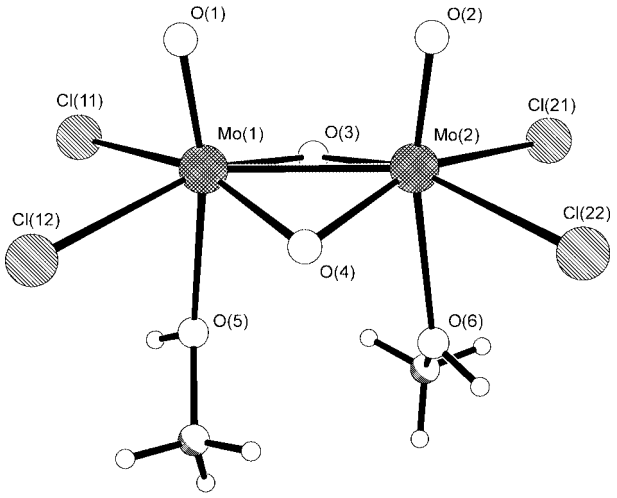



Figure 4. A drawing of the dinuclear $[Mo_2O_4Cl_4(MeOH)_2]^{2-}$ unit in **3** with the atom labelling scheme.

Table 3. Selected geometric parameters [Å; °] of the $[Mo_2O_4X_4(MeOH)_2]^{2-}$ (X = Cl, Br) ions in **3**, **4** and **5**.

| | **3** | **4** | **5** |
|---|---|---|---|
| Mo=O | 1.674(4), 1.679(4) | 1.6728(19) | 1.670(3) |
| Mo–O($\mu_2$) | 1.938(8)–1.949(4) | 1.9466(16)–1.9470(16) | 1.947(3), 1.953(3) |
| Mo–MeOH | 2.351(4), 2.372(4) | 2.3591(18) | 2.359(3) |
| Mo–X[a] | 2.4419(13)–2.4839(12) | 2.4462(6), 2.4765(6) | 2.5995(5), 2.6304(5) |
| Mo–O($\mu_2$)–Mo | 83.56(14), 83.64(14) | 83.53(6) | 83.01(10) |
| O($\mu_2$)–Mo–O($\mu_2$) | 91.60(15), 91.66(15) | 91.80(7) | 92.19(11) |
| Mo–Mo | 2.5902(6) | 2.5934(4) | 2.5841(6) |
| Fold angle[b] | 146.01(10) | 146.34(5) | 145.73(8) |

[a] X = Cl for **3** and **4**; X = Br for **5**. [b] As defined in the text.

dinated methanol molecules are oriented with their O–H termini pointing in the opposite directions. Although the entire anion belongs to the asymmetric unit, it comes very close to having $C_2$ symmetry.

### *Structures of the Orthorhombic Modifications of $(PyH)_2[Mo_2O_4Cl_4(MeOH)_2]$ (4) and $(PyH)_2[Mo_2O_4Br_4(MeOH)_2]$ (5)*

The structures of the orthorhombic modifications of $(PyH)_2[Mo_2O_4X_4(MeOH)_2]$ (X = Cl, Br) are isotypic. Only one half of the anion belongs to the asymmetric unit, the other half being generated by a crystallographic twofold rotation axis, which passes along the Mo=O vectors through the centre of the Mo($\mu_2$-O)$_2$Mo rhombus. The relevant geometric parameters for the inner coordination spheres for **4** and **5** are given in Table 3. The dimensions of the anion in **4** compare very well with those in **3**.

### *Comparison of the Structures of Triclinic (3) and Orthorhombic Modification of $(PyH)_2[Mo_2O_4X_4(MeOH)_2]$ [X = Cl (4) and X = Br (5)]*

The differences between the two modifications arise in the hydrogen-bonding pattern. The intermolecular hydrogen bonds are formed in both polymorphs between methanol and halo ligands. Two donors of hydrogen bonds in each anion, i.e., a pair of coordinated methanol molecules, are matched with two acceptors, two out of four halo ligands. Therefore each anion forms four hydrogen bonds, in the triclinic modification with two neighbouring anions, while in the orthorhombic modification with four. In the triclinic polymorph one chloro ligand, labelled Cl(11), and the methanol coordinated to the same molybdenum atom of the $\{Mo_2O_4\}^{2+}$ unit form two hydrogen bonds to the methanol and chloro ligand of the closest neighbouring anion (Figure 5), the corresponding O(5)···Cl(11)a distances are 3.176(4) Å [(*a*) 1 – *x*, –*y*, –*z*]. Similarly, Cl(22) and the methanol coordinated to the other molybdenum atom of the dinuclear anion also form two hydrogen bonds with their closest neighbour, the corresponding O(6)···Cl(22)b distances are 3.191(4) Å [(*b*) 2 – *x*, 1 – *y*, 1 – *z*]. A linkage of each anion with two neighbours produces infinite chains that propagate along the unit cell body diagonal. The engagement of two chloro ligands in hydrogen bonds accounts for the variations in the molybdenum-to-chlorine bond lengths: the chloro ligand involved in the hydrogen bond binds to molybdenum at a longer distance, i.e., Mo(1)–Cl(11) = 2.4839(12) Å and Mo(2)–Cl(22) = 2.4779(12) Å vs. Mo(1)–Cl(12) = 2.4419(13) Å and Mo(2)–Cl(21) = 2.4454(13) Å. In the orthorhombic polymorph each anion forms four hydrogen bonds, with lengths of 3.2925(18) Å, to four adjacent anions (Figure 6). Such a connectivity results in infinite layers parallel to the *ab* plane. The engagement of two out of four coordinated chloro ligands in hydrogen bonds is again reflected in the molybdenum-to-chlorine bond lengths, i.e., 2.4765(6) vs. 2.4462(6) Å. By analogy, **5** displays a non-equivalence of the molybdenum-to-bromine bond lengths, 2.6304(5) vs. 2.5995(5) Å.

It can also be observed that the molybdenum-to-chlorine bond lengths in **3** and **4** are similar to those determined for the aqua-ligated ion $[Mo_2O_4Cl_4(H_2O)_2]^{2-}$ [2.453(2) and 2.475(2) Å][21] or the very similar $[Mo_2O_4Cl_3(H_2O)_3]^-$ [2.434(2)–2.450(2) Å],[22] and are longer than in their base-free analogue, $[Mo_2O_4Cl_4]^{2-}$, where the distances are 2.392(6)–2.407(6) Å for the $[As(C_6H_5)_4]^+$ salt[23] or 2.352(4)–2.391(3) Å for $(Ph_3P{=}N{=}PPh_3)(Et_3NH)$-$[Mo_2O_4Cl_4]$.[24] The decrease in the bond lengths in the $[Mo_2O_4Cl_4]^{2-}$ ions with five-coordinate metal atoms is fully in agreement with the reasonable expectation of the increased bond strengths to other ligands when the sixth ligand is absent. The molybdenum-to-bromine bonds in **5** are longer than those determined for $[Mo_4O_8(OEt)_2Br_2Py_4]$ [2.5355(11)–2.5747(10) Å][12a] or mononuclear $(PyH)_5$-$[MoOBr_4(H_2O)]_3Br_2$ [2.498(4)–2.563(4) Å].[16]

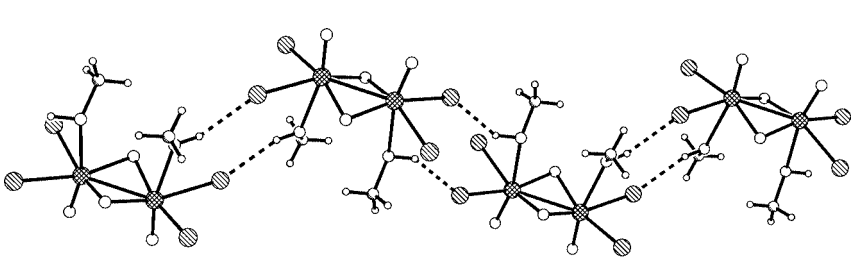


Figure 5. Hydrogen bonds in **3**: pairs of O(methanol)···Cl interactions link dinuclear anions into infinite chains.

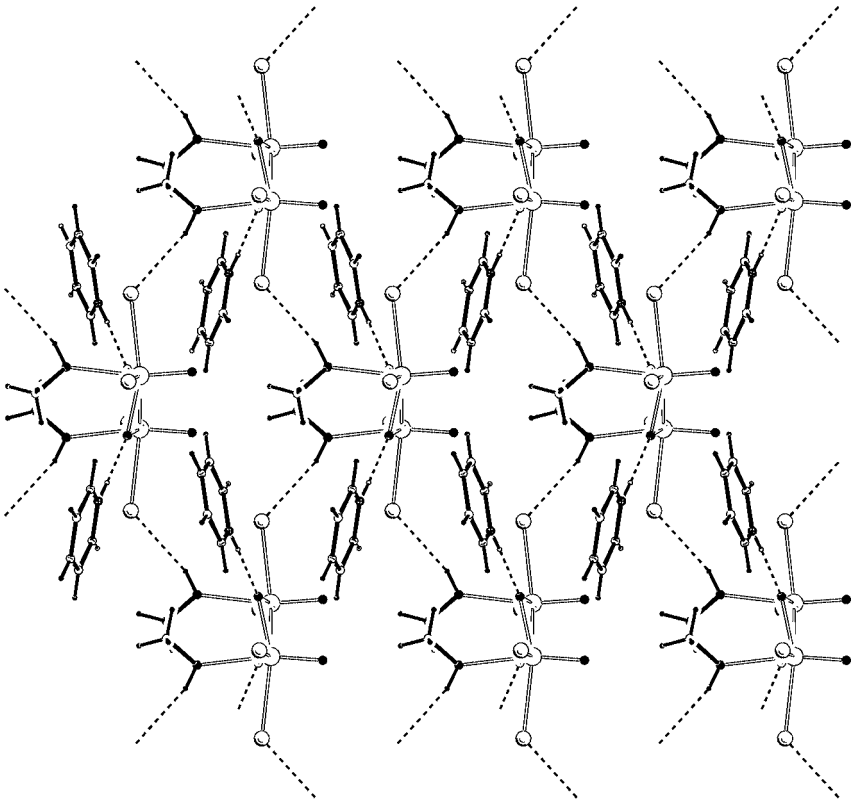


Figure 6. Hydrogen bonds in **4** and **5**: four O(methanol)···X interactions link each anion to four adjacent anions to form infinite layers perpendicular to the *c* axis.

The pyridinium cations are hydrogen bonded to the doubly-bridging oxygen atoms from the anions in both modifications (Figure 7). The corresponding N···O distances are 2.7001(60)–2.7031(62) Å for **3**, 2.6799(27) Å for **4** and 2.7329(45) Å for **5**.

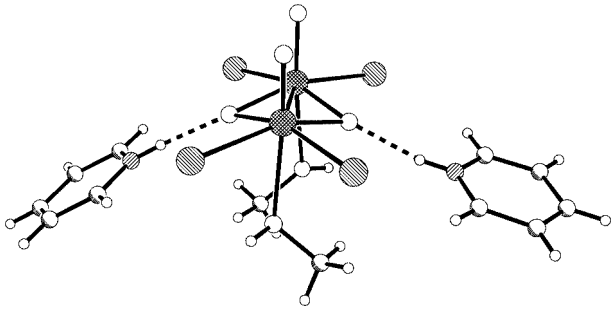


Figure 7. A dinuclear anion in **5** with a pair of hydrogen-bonded pyridinium cations.

### *Structure of $(PyH)_2[Mo_4O_8(OMe)_2(MeOH)_2Br_4]$ (6)*

The structure of compound **6** is similar to its three, already described, analogues $(PyH)_2[Mo_4O_8(OMe)_2(MeOH)_2Cl_4]$ and $(PyH)_2[Mo_4O_8(OEt)_2(EtOH)_2X_4]$ (X = Cl and Br).[12a] It consists of pyridinium cations and tetranuclear anions (Figure 8). Selected geometric parameters are given in Table 4. The centrosymmetric tetranuclear core may be envisioned as two $\{Mo_2O_4\}^{2+}$ units sharing a pair of bridging oxo groups and being linked, in addition, by two methoxide ions (Scheme 2). The six peripheral positions of the $\{Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OMe)_2\}^{2+}$ core are occupied by two methanol molecules at 2.2046(28) Å and four bromo ligands, two at shorter distances [2.5709(5) Å] and two at longer distances [2.5923(5) Å]. Methanol is engaged in a hydrogen-bonding interaction with the neighbouring bromo ligand at a distance of 3.2050(30) Å. This hydrogen bond contributes substantially to the stability of **6**. The hydrogen bond accounts for the variations in the molybdenum-to-bromine bond lengths. The pyridinium cations and the anionic clusters are linked, as observed before, through the agency of hydrogen bonds of moderate

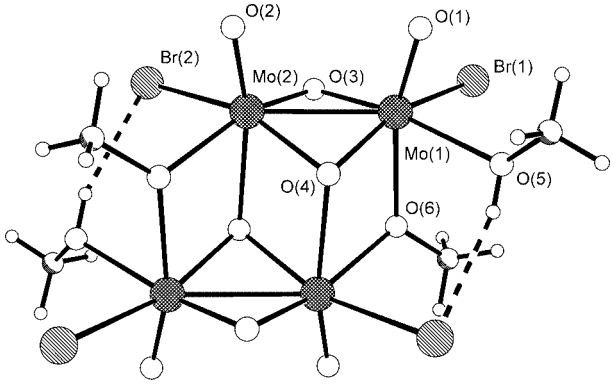



Figure 8. A drawing of the tetranuclear $[Mo_4O_8(OMe)_2(MeOH)_2Br_4]^{2-}$ unit in **6**. Hydrogen bonds between methanol and bromo ligands are drawn as dashed lines.

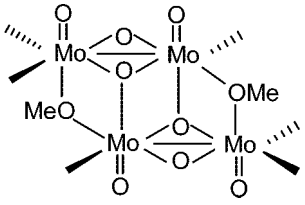
  

strength, localised between the pyridinium nitrogen and the doubly-bridging oxygen from the anion [N(1)···O(3) = 2.7928(47) Å].

Table 4. Relevant geometric parameters [Å; °] of the $[Mo_4O_8(OMe)_2(MeOH)_2Br_4]^{2-}$ ion in **6**.

| | |
|---|---|
| Mo–Mo | 2.5988(4) |
| Mo=O | 1.670(3), 1.679(3) |
| Mo–$O_b$[a] | 1.932(3)–1.990(3) |
| Mo–MeOH | 2.2046(28) |
| Mo–Br | 2.5709(5), 2.5923(5) |
| Mo–$O_b$–Mo | 81.77(10), 84.27(11) |
| $O_b$–Mo–$O_b$ | 93.04(11), 93.65(11) |
| Fold angle | 149.99(14) |
| O···Br[b] | 3.2050(30) |

[a] $O_b$ denotes bridging oxo groups in the $\{Mo_2O_4\}^{2+}$ unit: in a tetranuclear core one is formally a $\mu_2$- and the other a $\mu_3$-bridging ligand. [b] An intramolecular hydrogen bond between methanol and the neighbouring bromo ligand.




Scheme 2. A tetranuclear $\{Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OMe)_2\}^{2+}$ core.

## Comments on the Methanol Ligation

Structurally characterised alcohol complexes of molybdenum(V) are relatively rare. Invariably, these are all rather unstable species, in spite of the fact that in most cases the coordinated alcohol is involved in intra- or intermolecular hydrogen-bonding interactions through which some stability is gained. The only structurally characterised mononuclear complex is a very unstable $[MoOCl_3(EtOH)]$ with a square-pyramidal geometry and ethanol *cis* to the strongly bound terminal oxo group.[25] Likewise, the alcohol adopts *cis* positions with respect to the molybdenyl group in a series of dinuclear complexes with the composition $[Mo_2O_4L_2(ROH)_2]$ (L = β′-hydroxy-β-enaminone; R = Me, Et, *i*Pr),[26] tetranuclear $[(Mo_2O_4)_2(OMe)_2(MeOH)_2[HB(pz)_3]_2]$ [$HB(pz)_3^-$ = hydrotris(pyrazolyl)borate],[27] and octanuclear $[(Mo_2O_4)_4(OMe)_6(MeOH)_4Cl_2]$.[4] However, the position of ethanol in $[Mo_2O_2Cl_4(\mu_2\text{-}OEt)_2(\mu_2\text{-}EtOH)]$, where it also serves as a third bridge between metal atoms, is *trans* to both Mo=O groups.[28] The extreme reactivity of the latter complex was further exploited in the preparation of $[Mo_4O_6(OEt)_4(EtOH)_2Cl_4]$[24] and $[Mo_8O_{12}(OH)_6(OEt)_4(EtOH)_4Cl_6]$,[29] which both retain ethanol ligands on their periphery. The methanol ligands in the anions of $(PyH)_2[MoOCl_4(MeOH)]Cl$ (**2**), $(PyH)_2[Mo_2O_4Cl_4(MeOH)_2]$ (**3** and **4**) and $(PyH)_2[Mo_2O_4Br_4(MeOH)_2]$ (**5**) are *trans* to the terminal oxo groups. Owing to the *trans* influence of the latter, the methanol ligand binds at a longer distance. The corresponding bond in **2** is somewhat short taking into account its position. Comparison of the molybdenum-to-alcohol bond lengths in various molybdenum(V) compounds (Table 5) reveals that these can be as long as 2.49 Å or as short as 2.10 Å. The former describes a situation with the alcohol ligand in *trans*, and the latter with the alcohol ligand in the *cis* position with respect to the Mo=O group.

Table 5. Molybdenum-to-alcohol bond lengths [Å] in a series of molybdenum(V) compounds.[a]

| | Mo–ROH |
|---|---|
| **2** | 2.2911(5) |
| **3** | 2.351(4), 2.372(4) |
| **4** | 2.3591(18) |
| **5** | 2.359(3) |
| **6** | 2.2046(18) |
| $[Mo_2O_4L_2(MeOH)_2]$[26] | 2.199(2), 2.201(2) |
| $[(Mo_2O_4)_2(OMe)_2(MeOH)_2[HB(pz)_3]_2]$[27] | 2.264(3) |
| $[(Mo_2O_4)_4(OMe)_6(MeOH)_4Cl_2]$[4] | 2.084, 2.195[b] |
| $(PyH)_2[Mo_4O_8(OMe)_2(MeOH)_2Cl_4]$[12a] | 2.2070(13) |
| $(PyH)_2[Mo_4O_8(OEt)_2(EtOH)_2Cl_4]$[12a] | 2.2025(19) |
| $(PyH)_2[Mo_4O_8(OEt)_2(EtOH)_2Br_4]$[12a] | 2.2007(22) |
| $[MoOCl_3(EtOH)]$[25] | 2.102(2) |
| $[Mo_4O_6(OEt)_4(EtOH)_2Cl_4]$[24] | 2.144(4) |
| $[Mo_2O_2Cl_4(\mu_2\text{-}OEt)_2(\mu_2\text{-}EtOH)]$[28] | 2.470(6)–2.495(6) |

[a] See text for the positions of the alcohol ligands with respect to the Mo=O group. [b] Bond lengths are taken from the CCDC.[30]

## Vibrational Spectroscopy

The presence of a terminal metal–oxygen double bond can be correlated with a stretching frequency in the range 1020–940 $cm^{-1}$.[3,31] The spectrum of $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ (**1**) reveals a strong absorption at 982 $cm^{-1}$. A related compound, the bis(ethylenedithio)tetrathiafulvalene salt of $[MoOCl_4(H_2O)]^-$, displays the Mo=O stretch at 974 $cm^{-1}$.[17b] The spectra of compounds **2**, **3**, **5** and **6** display several strong bands in the region of 990–950 $cm^{-1}$ which are associated with the Mo=O stretching frequencies.

The alcohol O–H stretching vibration is known to be sensitive to the involvement of the alcohol in hydrogen bonds. As a result, the band is shifted into a lower frequency region, to about 3300 $cm^{-1}$.[32] The spectrum of $(PyH)_2[Mo_4O_8(OMe)_2(MeOH)_2Br_4]$ (**6**) reveals a weak absorption at 3259 $cm^{-1}$, which may be attributed to the O–H stretching vibration. A band of medium intensity in a higher frequency region, at 3443 and 3431 $cm^{-1}$, is displayed in the spectra of $(PyH)_2[Mo_2O_4Cl_4(MeOH)_2]$ (**3**) and $(PyH)_2[Mo_2O_4Br_4(MeOH)_2]$ (**5**), respectively. Similarly, the O–H stretching mode in the spectrum of $[MoOCl_3(EtOH)]$ is also found at 3413 $cm^{-1}$.[25] Since considerable difficulties were experienced in recording the spectrum of $(PyH)_2[MoOCl_4(MeOH)]Cl$ (**2**), due to its decomposition, no conclusive assignments can be based upon it. Absorptions at 1002 $cm^{-1}$ for **3**, 1003 $cm^{-1}$ for **5** and 1026 $cm^{-1}$ for **6** may be assigned to the C–O stretching vibrations. Their frequencies are consistent with the normally observed range (1075–1000 $cm^{-1}$).[32] The spectra of all methanol complexes, with **2** included, display a band of medium intensity in a narrow frequency range of 878–851 $cm^{-1}$. This absorp-

tion was tentatively ascribed to the methyl rocking vibration.

### The Starting Oxohalomolybdates(V)

Although the simple oxohalomolybdates(v), i.e., the six-coordinate, octahedral $[MoOX_5]^{2-}$, $[MoOX_4L]^-$ and five-coordinate, square-pyramidal $[MoOX_4]^-$ (X = F, Cl, Br, I and L = $H_2O$, THF etc.) have been extensively studied for more than a century,[33] as far as our starting materials, $(PyH)_2[MoOCl_5]$ and $(PyH)[MoOBr_4]$, are concerned, neither their true identities nor their structures were known. The formulation of the former as $(PyH)_2[MoOCl_5]$ was clearly erroneous, as shown by the X-ray structure analysis of **1** which has disclosed that it consists of $[MoOCl_4(H_2O)]^-$ and not $[MoOCl_5]^{2-}$ ions. Since $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ (**1**) was isolated from hydrochloric acid, this result is not surprising in view of the previous finding that the species formed on dissolving $(Et_4N)_2[MoOCl_5]$ or $[MoOCl_3]$ in concentrated aqueous hydrochloric acid is $[MoOCl_4(H_2O)]^-$ and not $[MoOCl_5]^{2-}$,[34] as generally supposed.

Contrary to the well-defined geometry of $[MoOX_4L]^-$ ions, there has been considerable ambiguity concerning the structures of the base-free $[MoOX_4]^-$ ions. The metal displays a marked tendency to extend its coordination number to six, for instance by coordinating to water, so the square-pyramidal $[MoOX_4]^-$ ions are unstable in the presence of moisture, unless protected by bulky cations.[35] The sixfold coordination can also be achieved through straight Mo=O···Mo or bent Mo–X···Mo interactions, which result in pair-wise associations or infinite chains. Isopropylideneiminium[36] and trifluoroacetamidinium[37] salts of $[MoOCl_4]^-$ actually exist in the solid state as dimeric $[MoOCl_4]_2^{2-}$ anions where two asymmetric chloro bridges link a pair of molybdenum atoms. In the infinite anionic chains of $[Te_{15}X_4]_n[MoOX_4]_{2n}$ (X = Cl, Br), short, formally Mo=O double bonds with lengths of about 1.63 Å alternate with weaker, longer Mo–O bonds with lengths of around 2.41 Å.[38] On the other hand, the linkage of square-pyramids via asymmetric chloro bridges in $K[MoOCl_4]$ produces infinite zig-zag chains.[39] The presence of the sixth ligand, for instance base L in $[MoOX_4L]^-$, has the effect of altering the strength of the Mo=O bond, and this is reflected in the position of the Mo=O stretching frequency.[40] Consequently, the shift in the Mo=O stretching frequency due to the Mo=O···Mo interaction is even more pronounced. The absorption at 883 $cm^{-1}$ in the infrared spectrum of $(PyH)[MoOBr_4]$ strongly indicates a polymeric chain structure via Mo=O···Mo interactions.[13,41] Support for this also comes from the infrared spectrum of $(PyH)_2[Mo_2O_4Cl_4]\cdot 3H_2O$ whose X-ray structure reveals chains of dinuclear $[Mo_2O_4Cl_4]^{2-}$ ions linked via Mo=O···Mo interactions.[42] The Mo–O stretching band for $(PyH)_2[Mo_2O_4Cl_4]\cdot 3H_2O$ is observed at 888 $cm^{-1}$.

### Synthetic Considerations

The green colour of the solution obtained upon dissolving $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ (**1**) in methanol does not suggest a substantial extent of dimerisation. Undisputedly, the first reaction upon dissolving the $[MoOCl_4(H_2O)]^-$ ion in methanol is the substitution of the coordinated water for methanol, which is present in huge excess. The product of this reaction, $[MoOCl_4(MeOH)]^-$, is a labile species, which reacts with atmospheric moisture almost instantaneously. If the solution whose preparation is described in the synthetic procedure for **2** is exposed to air after the addition of diethyl ether, it undergoes a rapid colour change from green to orange. The evaporation of solvents in air produces a substantial amount of orange crystals, which were identified by X-ray diffraction as a triclinic modification of $(PyH)_2[Mo_2O_4Cl_4(MeOH)_2]$ (**3**), within a couple of hours. Overnight evaporation leaves behind a solid residue which consists mainly of large, needle-like crystals of the starting material $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ (**1**), and an unidentified, dark blue, amorphous phase. The taking-up of water from the atmosphere by $[MoOCl_4(MeOH)]^-$ and the subsequent deposition of $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ (**1**) as the final product, is not surprising. As far as the formation and the fate of the intermediate product, $(PyH)_2[Mo_2O_4Cl_4(MeOH)_2]$ (**3**), are concerned, both are unclear. Bearing in mind that no substantial dimerisation takes place in methanol, it is likely that water from the atmosphere triggers the dimerisation. Since $[Mo_2O_4Cl_4(MeOH)_2]^{2-}$ still possesses labile sites, four chloro and two methanol ligands, further substitution reactions are initiated and accompanied by partial oxidation to the +6 oxidation state, which results in a blue material. Addition of a stoichiometric amount of pyridine or trifluoroacetate to a methanol solution of $[MoOCl_4(H_2O)]^-$ was shown to promote the dimerisation and $(PyH)_2[Mo_2O_4Cl_4(MeOH)_2]$ (**3** and **4**) was isolated. On prolonged reaction times further assembly of $\{Mo_2O_4\}^{2+}$ units into $\{Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OMe)_2\}^{2+}$ core (Scheme 2), found in the final product $(PyH)_2[Mo_4O_8(OMe)_2(MeOH)_2Cl_4]$, was observed. The latter process can be avoided by keeping the reaction temperature at 5 °C. Addition of a larger amount of pyridine yields $[Mo_4O_8(OMe)_2Cl_2Py_4]$. Pyridine advances the assembly of dinuclear units and once its concentration is high enough, it coordinates to four out of six terminal positions of the $\{Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OMe)_2\}^{2+}$ core.

With the greater lability of the coordinated bromo ligands, the chances of isolating one of the more reactive intermediates are significantly smaller. Rather, the substitution tends to proceed further than in the case of the chloro starting material. Accordingly, the mononuclear $[MoOBr_4(MeOH)]^-$ could not be isolated under analogous conditions to those employed for $[MoOCl_4(MeOH)]^-$. $(PyH)_2[Mo_2O_4Br_4(MeOH)_2]$ (**5**) can only be isolated at 5 °C after the addition of trifluoroacetate to the methanol solution. At room temperature, further assembly of dinuclear subunits takes place with the formation of $(PyH)_2[Mo_4O_8(OMe)_2(MeOH)_2Br_4]$ (**6**) as the final product. The greater reactivity of the bromo-coordinated species is also demonstrated by the reaction where a small amount of pyridine was added to a methanol solution of $(PyH)[MoOBr_4]$, which produced $(PyH)_2[Mo_4O_8(OMe)_2(MeOH)_2Br_4]$ (**6**)

even at low temperature. $(PyH)_2[Mo_4O_8(OMe)_2(MeOH)_2Br_4]$ (**6**) is the first relatively stable bromo-coordinated species.

Similar compounds to ours have been obtained under strictly anhydrous conditions and temperatures as low as –78 °C from reactions of molybdenum(v) chloride in methanol.[43] The methanolysis of the Mo–Cl bonds was proposed to take place in step with successive formation of Mo=O bonds.[44] The formulae of the products, inferred from the elemental analysis data, are highly reminiscent of our methanol complexes. In particular, this applies to the green product of the reaction of $MoOCl_3$·2MeOH with pyridinium chloride in methanol at –78 °C, formulated as (PyH)[$MoOCl_4$]·MeOH, and the red, crystalline (PyH)[$MoO_2Cl_2$]·MeOH obtained from the reaction of $MoCl_5$ with pyridine in methanol.[43] The composition of the former resembles that of $(PyH)_2[MoOCl_4(MeOH)]Cl$ (**2**), while the composition of the latter is the same as for $(PyH)_2[Mo_2O_4Cl_4(MeOH)_2]$ (**3**). The lack of spectroscopic data precludes unambiguous conclusions about their true identity, although it can be reasonably expected that both molybdenum(v) chloride and $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ (**1**) would react in methanol with the formation of species with, if not exact, at least similar compositions. Irrespective of the starting material, the reactive fragments released in the first stages of the reaction reassemble with the formation of the most stable and least soluble species under the given conditions. In a more recent study of the molybdenum(v) chloride reactions in rigorously dried ethanol, $[MoOCl_3(EtOH)]$, H[$MoOCl_4$]·2EtOH,[25] and $[Mo_2O_2Cl_4(\mu_2\text{-}OEt)_2(\mu_2\text{-}EtOH)]$,[28] were isolated as the very first products, as confirmed by X-ray diffraction analyses. $[Mo_2O_2Cl_4(\mu_2\text{-}OEt)_2(\mu_2\text{-}EtOH)]$, which possesses several good leaving groups, reacts readily to form $[Mo_2O_4Cl_4]^{2-}$ and a series of $\{Mo_2O_2(\mu_2\text{-}O)(\mu_2\text{-}OEt)\}^{3+}$-containing clusters.[24,29] Interestingly, the same structural types are encountered within the $\{Mo_2O_2(\mu_2\text{-}O)(\mu_2\text{-}OEt)\}^{3+}$ clusters as in the larger group of $\{Mo_2O_4\}^{2+}$ clusters. Moreover, hydrogen chloride and chloroethane were found to be side products in the ethanolysis of Mo–Cl bonds. The proposed mechanisms of the formation of Mo–O and Mo–OR bonds cannot be applied to our reaction system as no attempts were made to avoid traces of water. In view of the high susceptibility of $[MoOX_4]^-$ and $[MoOX_4L]^-$ species towards hydrolysis, the role of water inherently present in the used solvents has to be acknowledged. The comparison with the two above-mentioned systems is therefore limited to the nature of the obtained products only.

## Conclusions

Facile substitution chemistry of mononuclear $[MoOCl_4(H_2O)]^-$ or polymeric $[MoOBr_4]_n^{n-}$ in methanol solutions has afforded a series of novel molybdenum(v) complexes with coordinated methanol: a mononuclear anion in $(PyH)_2[MoOCl_4(MeOH)]Cl$ (**2**), a dinuclear $\{Mo_2O_4\}^{2+}$-based anion in $(PyH)_2[Mo_2O_4Cl_4(MeOH)_2]$, which crystallises in a triclinic (**3**) and in an orthorhombic (**4**) unit cell, an analogous bromo-coordinated dinuclear anion in $(PyH)_2[Mo_2O_4Br_4(MeOH)_2]$ (**5**) and a tetranuclear anion built of two $\{Mo_2O_4\}^{2+}$ subunits in $(PyH)_2[Mo_4O_8(OMe)_2(MeOH)_2Br_4]$ (**6**). The coordinated methanol molecule invites further investigations as a potentially functional and highly labile group. Such studies are underway.

## Experimental Section

**General Remarks:** Reagents were purchased from Aldrich. No precaution was taken to eliminate traces of moisture present in solvents. The IR spectra were measured on solid samples as Nujol or poly(chlorotrifluoroethylene) mulls using a Perkin–Elmer 2000 series FT-IR spectrometer. Elemental analyses were performed by the Chemistry Department service at the University of Ljubljana. Molybdenum was determined as $PbMoO_4$ and halide by potentiometric titration with a 0.100 M solution of $AgNO_3$.

**(PyH)[$MoOBr_4$]:** Finely powdered $(NH_4)_2[MoBr_5(H_2O)]$[45] (2.75 g, 5.0 mmol) was added to a mixture of pyridine (0.8 mL) and conc. hydrobromic acid (25 mL). The solution was gently heated at about 80 °C until all solid material had been consumed. Hydrazinum dichloride (0.50 g, 4.76 mmol) was added and the reaction mixture was heated for another five minutes. Meanwhile its colour changed from brown to yellow-red. The obtained solution was left to stand at ambient conditions. The red, block-shaped, crystals that formed overnight were filtered off and washed with hexanes. Yield: 32% (820 mg, 1.6 mmol). IR: $\tilde{\nu}$ = 1627 $cm^{-1}$ (s), 1597 (vs), 1530 (vvs), 1321 (s), 1229 (w), 1195(m), 1164 (m), 1047 (m), 974 (w), 883 (vvs), 747 (m), 731 (vvs), 664 (vvs). $C_5H_6Br_4MoNO$ (511.65): calcd. C 11.74, H 1.18, Br 62.47, Mo 18.75, N 2.74; found C 11.51, H 1.30, Br 62.3, Mo 18.6, N 2.69.

**$(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ (1):** This synthetic procedure combines two literature approaches to related compounds.[46] A mixture of conc. hydrochloric acid (12.5 mL) and hydriodic acid (3.5 mL) was added to a 1.0 M solution of molybdenum(VI) oxide in conc. hydrochloric acid (25 mL). The reaction mixture was heated in an open flask until all iodine had been driven off. A mixture of pyridine (6.3 mL) and conc. hydrochloric acid (35 mL) was added, the flask was stoppered and left in an ice bath for two hours. Emerald-green, needle-shaped crystals of **1** were filtered off and washed with hexanes. Yield: 82% (8.80 g, 6.84 mmol). IR: $\tilde{\nu}$ = 3195 $cm^{-1}$ (w), 3146 (w), 3126 (w), 3088 (w), 1631 (m), 1598 (vs), 1525 (vs), 1237 (m), 1196 (m), 1164 (m), 1078 (w), 1047 (m), 1027 (w), 982 (vvs), 905 (m), 749 (vvs), 722 (m), 677 (vvs). $C_{25}H_{36}Cl_{14}Mo_3N_5O_6$ (1286.7): calcd. C 23.34, H 2.82, Cl 38.57, Mo 22.37, N 5.44; found C 23.45, H 2.74, Cl 38.4, Mo 22.3, N 5.37.

**$(PyH)_2[MoOCl_4(MeOH)]Cl$ (2):** $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ (**1**; 400 mg, 0.311 mmol) was dissolved in methanol (4.0 mL). The solution was kept in a stoppered Erlenmeyer flask at ambient conditions overnight. Diethyl ether (8.5 mL) was added dropwise with constant stirring. After the addition of diethyl ether, the colour of the solution changed from yellow-green to light-green. Within one hour large, plate-like crystals of **2** started to grow from the solution. *Note.* The crystals of **2** decompose almost instantaneously when taken out from the mother liquor. IR: $\tilde{\nu}$ = 3207 $cm^{-1}$ (w), 3145 (w), 1632 (m), 1599 (s), 1526 (s), 1322 (m), 1237 (m), 1190 (m), 1164 (m), 1079 (w), 1050 (m), 1056 (m), 1030 (m), 982 (s), 962 (vs), 851 (m), 748 (vs), 729 (vs), 669 (vs), 608 (s).

**Triclinic (3) and Orthorhombic (4) Modifications of $(PyH)_2[Mo_2O_4Cl_4(MeOH)_2]$. Procedure a:** $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ (**1**; 400 mg, 0.311 mmol) was dissolved in methanol (4.0 mL). Pyridine (1.20 mmol; 2.4 mL of a 0.50 M pyridine solution in methanol) was added to the solution. The colour changed immediately from yellow-green to brown-orange. The Erlenmeyer flask was stoppered and left at ambient conditions for three hours. Orange crystals of **3** could then be filtered off. Yield: 40% (116 mg, 0.187 mmol). IR: $\tilde{\nu}$ = 3611 $cm^{-1}$ (w), 3552 (w), 3443 (m), 3411 (w), 3129 (w), 3107 (w), 3082(w), 3059 (w), 1634 (m), 1615 (m), 1592 (m), 1541 (m), 1484 (vvs), 1253 (m), 1200 (s), 1167 (m), 1103 (m), 1095 (w), 1061 (w), 1051 (w), 1002 (vvs), 986 (vvs), 964 (vvs), 950 (m), 878 (m), 760 (vs), 750 (vvs), 743 (vvs), 735(vvs), 728 (vvs), 681 (vs), 607 (s), 503 (s). *Note.* If the reaction mixture was left at ambient conditions overnight, red, block-like crystals formed. The product revealed an infrared spectrum identical to that described for $(PyH)_2[Mo_4O_8(OMe)_2(MeOH)_2Cl_4]$.[12a] Yield: 41% (91 mg, 0.097 mmol). IR: $\tilde{\nu}$ = 3232 $cm^{-1}$ (m), 3159 (w), 3129 (w), 3105 (w), 3085 (w), 3062 (w), 1635 (vs), 1610 (vvs), 1537 (vvs), 1251 (m), 1201 (s), 1164 (s), 1113 (m), 1032 (vvs), 1002 (vvs), 966 (vvs), 946 (vvs), 878 (w), 755 (vvs), 725 (vvs).

**Procedure b:** Pyridinium trifluoroacetate (1.20 mmol; 1.0 mL of a 1.20 M solution in acetonitrile) was added to methanol (4.0 mL). $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ (**1**; 400 mg, 0.311 mmol) was dissolved in this solution. The orange-brown reaction mixture was left in a closed flask at ambient conditions overnight. A vial containing diethyl ether (2.5 mL) was carefully placed into the flask on the following day. The flask was stoppered and placed in the refrigerator. Orange, rhombic crystals of $(PyH)_2[Mo_2O_4Cl_4(MeOH)_2]$ (triclinic modification **3**) and red, block-shaped crystals of $(PyH)_2[Mo_2O_4Cl_4(MeOH)_2]$ (orthorhombic modification **4**) grew from the solution within 24 hours.

**Addition of a Larger Amount of Pyridine to a Methanol Solution of $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ (1):** $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ (**1**; 400 mg, 0.311 mmol) was dissolved in methanol (4.0 mL). After the addition of 12.3 mmol of pyridine (1.0 mL) to the yellow-green solution, its colour changed to brown-orange. The Erlenmeyer flask was stoppered and left at ambient conditions for five hours. A red, crystalline product was filtered off and washed with hexanes. The product revealed an infrared spectrum identical to that described for $[Mo_4O_8(OMe)_2Cl_2Py_4]$.[12f] Yield: 91% (205 mg, 0.213 mmol). IR: $\tilde{\nu}$ = 3391 $cm^{-1}$ (m), 3067 (w), 2788 (m), 1636 (w), 1607 (vvs), 1571 (w), 1540 (w), 1362 (w), 1303 (w), 1246 (w), 1222 (vs), 1164 (m), 1154 (m), 1076 (vvs), 1044 (vvs), 1024 (vvs), 954 (vvs), 933 (vvs), 921 (vvs), 875 (w), 757 (vvs), 744 (vvs).

**$(PyH)_2[Mo_2O_4Br_4(MeOH)_2]$ (5):** Pyridinium trifluoroacetate (1.20 mmol; 1.0 mL of a 1.20 M solution in acetonitrile) was added to methanol (4.0 mL) in an Erlenmeyer flask. $(PyH)[MoOBr_4]$ (480 mg, 0.94 mmol) was dissolved in this solution. The orange-red solution was immediately placed in the refrigerator (5 °C). Diethyl ether (2.5 mL) was carefully added to the solution on the following day. The reaction mixture was placed back in the refrigerator and after two days a second portion of diethyl ether (4.5 mL) was added. Red, block-shaped crystals of **5** appeared within six hours. *Note.* The crystals are not stable outside the mother liquor. IR: $\tilde{\nu}$ = 3611 $cm^{-1}$ (w), 3563 (w), 3431 (m), 3127 (w), 3101 (w), 3083 (w), 3062 (m), 3059 (w), 2924 (m), 2856 (m), 1625 (vs), 1613 (vs), 1592 (s), 1537 (s), 1483 (vs), 1253 (w), 1200 (m), 1194 (m), 1164 (m), 1093 (w), 1060(m), 1051 (m), 1003 (s), 971 (vvs), 953 (vs), 876 (w), 755 (vs), 718 (vvs), 679 (vs), 606 (s), 490 (s).

**$(PyH)_2[Mo_4O_8(OMe)_2(MeOH)_2Br_4]$ (6). Procedure a:** The same procedure was used as for the preparation of compound **5**, only the reaction mixture was left to stand at ambient conditions. Pyridinium trifluoroacetate (1.20 mmol; 1.0 mL of a 1.20 M solution in acetonitrile) was added to methanol (4.0 mL) in an Erlenmeyer flask. $(PyH)[MoOBr_4]$ (480 mg, 0.94 mmol) was dissolved in this solution. The flask was stoppered and the orange-red reaction mixture was left to stand at ambient conditions for two days. A vial containing diethyl ether (5.0 mL) was carefully inserted into the flask. The flask was tightly stoppered and left at ambient conditions for two more days. Red, block-shaped crystals of **6** were filtered off and washed with hexanes. Yield: 53% (140 mg, 0.125 mmol).

**Procedure b:** $(PyH)[MoOBr_4]$ (480 mg, 0.94 mmol) was dissolved in methanol (4.0 mL) and pyridine (1.20 mmol; 2.4 mL of a 0.50 M solution in methanol) was then added. The orange-red solution was left at ambient conditions. A vial with diethyl ether (5.0 mL) was carefully inserted into the Erlenmeyer flask on the following day. Red, block-shaped crystals formed within two days. The product was filtered off and washed with hexanes. Yield: 39% (103 mg, 0.0921 mmol). *Note.* The same product, $(PyH)_2[Mo_4O_8(OMe)_2(MeOH)_2Br_4]$ (**6**), was obtained if the reaction mixture was kept at 5 °C the whole time. IR: $\tilde{\nu}$ = 3259 $cm^{-1}$ (m), 3135 (w), 3132 (w),

Table 6. Crystallographic data for compounds **1**–**6**.

| | **1** | **2** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|---|
| Empirical formula | $C_{25}H_{36}Cl_{14}Mo_3N_5O_6$ | $C_{11}H_{16}Cl_5MoN_2O_2$ | $C_{12}H_{20}Cl_4Mo_2N_2O_6$ | $C_{12}H_{20}Cl_4Mo_2N_2O_6$ | $C_{12}H_{20}Br_4Mo_2N_2O_6$ | $C_{14}H_{26}Br_4Mo_4N_2O_{12}$ |
| Formula mass | 1286.7 | 481.45 | 621.98 | 621.98 | 799.82 | 1117.77 |
| Crystal system | orthorhombic | monoclinic | triclinic | orthorhombic | orthorhombic | triclinic |
| Space group | *Pmma* | $P2_1/n$ | $P\bar{1}$ | *Pcan* | *Pcan* | $P\bar{1}$ |
| $T$ [K] | 200(2) | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) |
| $a$ [Å] | 21.4445(2) | 7.35420(10) | 8.3525(2) | 8.25560(10) | 8.32140(10) | 9.2712(2) |
| $b$ [Å] | 8.06490(10) | 33.3209(4) | 9.7414(2) | 14.0632(2) | 14.4784(3) | 9.5517(2) |
| $c$ [Å] | 13.34650(10) | 7.88750(10) | 14.7231(4) | 17.9084(2) | 18.3149(4) | 9.8151(2) |
| $\alpha$ [°] | 90 | 90 | 93.3055(11) | 90 | 90 | 111.1186(9) |
| $\beta$ [°] | 90 | 104.6646(5) | 104.1614(11) | 90 | 90 | 113.3588(9) |
| $\gamma$ [°] | 90 | 90 | 114.5058(12) | 90 | 90 | 94.5516(11) |
| $V$ [Å$^3$] | 2308.25(4) | 1869.86(4) | 1039.57(4) | 2079.17(5) | 2206.59(7) | 718.86(3) |
| $Z$ | 2 | 4 | 2 | 4 | 4 | 1 |
| $\lambda$ [Å] | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| $\mu$ [mm$^{-1}$] | 1.654 | 1.418 | 1.750 | 1.750 | 8.408 | 7.318 |
| Collected reflections | 5190 | 7467 | 7955 | 4409 | 4467 | 5829 |
| Unique reflections, $R_{int}$ | 2905, 0.0110 | 4174, 0.0142 | 4544, 0.0206 | 2359, 0.0081 | 2460, 0.0305 | 3149, 0.0258 |
| Observed reflections | 2512 | 3974 | 4370 | 2257 | 2200 | 2871 |
| $R1$ [$I > 2\sigma(I)$] | 0.0298 | 0.0232 | 0.0416 | 0.0243 | 0.0342 | 0.0287 |
| $wR2$ [all data] | 0.0754 | 0.0789 | 0.1217 | 0.0587 | 0.0873 | 0.0761 |

3103 (w), 3082 (w), 3060 (m), 1635 (s), 1609 (s), 1536 (vs), 1485 (vvs), 1429 (m), 1369 (m), 1250 (m), 1202 (s), 1162 (s), 1106 (m), 1053 (m), 1026 (vvs), 994 (vvs), 965 (vvs), 946 (vvs), 876 (w), 752 (vvs), 724 (vvs), 674 (vvs), 639 (w), 608 (s). $C_{14}H_{26}Br_4Mo_4N_2O_{12}$ (1117.8): calcd. C 15.04, H 2.34, Br 28.60, Mo 34.33, N 2.51; found C 15.12, H 2.42, Br 28.75, Mo 34.2, N 2.45.

**X-ray Crystallographic Study:** The crystals were mounted on the tip of a glass fibre with a small amount of silicon grease and transferred to a goniometer head. Data were collected with a Nonius Kappa CCD diffractometer. For all compounds, data reduction and integration were performed with the software package DENZO-SMN.[47] Averaging of the symmetry-equivalent reflections largely compensated for the absorption effects. The coordinates of some or all of the non-hydrogen atoms were found by direct methods using the structure solution program SHELXS.[48] The positions of the remaining non-hydrogen atoms were located by use of a combination of least-squares refinement and difference Fourier maps with the SHELXL-97 program.[48] Non-hydrogen atoms were refined with anisotropic displacement parameters. The water hydrogen atoms in **1**, hydroxyl methanol hydrogen atoms in **2**, **3**, **4** and **5** located in the final stages of the refinement from the difference Fourier maps were refined with isotropic displacement parameters. The remaining hydrogen atoms were included in the structure-factor calculations at idealised positions. Cell parameters and refinement results for compounds **1**–**6** are summarised in Table 6. Figures depicting the structures were prepared using SHELXTL[49] and PLATON.[50] CCDC-248502 (for **1**), -248503 (for **2**), -248504 (for **3**), -248505 (for **4**), -248506 (for **5**) and -248507 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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