Anions of 1,3,5-Benzenetricarboxylic and Heptanedioic Acids Serving as Bridges between Dimolybdenum(V) Metal–Metal Bonded Units: Preparation and Structural Characterization of Dinuclear and Tetranuclear Complexes

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$(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ and $(PyH)[MoOBr_4]$ reacted with the anions of 1,3,5-benzenetricarboxylic acid ($btcH_3$) and heptanedioic acid ($hdaH_2$) to afford a series of novel carboxylato complexes based on the $\{Mo_2O_4\}^{2+}$ structural core: $(PyH)_4[Mo_2O_4Cl_4(\mu_2\text{-}btcH_2)]Cl$ (**1**), $(PyH)_4[Mo_2O_4Br_4(\mu_2\text{-}btcH_2)]Br$ (**2**), $[(Mo_2O_4Py_3)_2(\mu_3\text{-}btcH)_2]\cdot 6Py$ (**3**), $(PyH)_6[(Mo_2O_4Cl_4)_2(\mu_4\text{-}hda)]\cdot 2CH_3CN$ (**4**), and $(PyH)_{10}[(Mo_2O_4Cl_4)_2(\mu_4\text{-}hda)][MoOCl_5]Cl_2$ (**5**) {Py = pyridine, C_5H_5N; PyH^+ = pyridinium cation, $C_5H_5NH^+$; $btcH_2^-$ = $(HOOC)_2C_6H_3COO^-$; $btcH^{2-}$ = $(HOOC)C_6H_3(COO)_2^{2-}$ and hda^{2-} = $^-OOC(CH_2)_5COO^-$}. A pair of isostructural compounds **1** and **2** contains dinuclear anions $[Mo_2O_4X_4(\mu_2\text{-}btcH_2)]^{3-}$ (X = Cl, Br) in which the $btcH_2^-$ ligand is bonded to the $\{Mo_2O_4\}^{2+}$ core via one carboxylate group in a *syn*-*syn* bidentate bridging manner. In **3**, two $btcH^{2-}$ ligands link two $\{Mo_2O_4\}^{2+}$ cores into a loop-like structure. Each $btcH^{2-}$ ligand is coordinated via two carboxylate groups, with one in the *syn*-*syn* bidentate bridging manner and with another in a monodentate manner. The linkage of two dinuclear subunits was also realized in $[(Mo_2O_4Cl_4)_2(\mu_4\text{-}hda)]^{6-}$, the anion in **4** and **5**, where both carboxylate groups of the hda^{2-} ligand bind in the *syn*-*syn* bidentate-bridging manner to $\{Mo_2O_4\}^{2+}$ cores. The title compounds were characterized by X-ray crystallography and infrared spectroscopy.

Introduction

The use of labile metal cations and polyfunctional organic molecules in the assembly of supramolecular arrays has emerged as an area of great interest.[1] In this context, di- and tricarboxylates constitute one of the most commonly employed classes of organic ligands.[2] The anions of 1,3,5-benzenetricarboxylic acid with three symmetrically arranged carboxylate groups form rigid, planar linkers.[3] By contrast, the ligands derived from dicarboxylic acids such as heptanedioic acid possess flexibility, an advantageous property in certain cases.[4] The metal cations such as Cu^{II}, Cd^{II}, Zn^{II}, Co^{II}, and Ni^{II} often do not impose a strong preference for a given geometry, leading to the lack of predictability over the stoichiometry and the structure of the product. On the contrary when dimolybdenum(II) precursors were used, both the number of coordinative sites and their locations could be suitably chosen in order to produce in combination with organic linkers a variety of supramolecular complexes.[5] Our quest has been the preparation of complexes containing a dinuclear $\{Mo_2O_4\}^{2+}$ structural core (Scheme 1). The core consists of two metal atoms, each with a strongly bound terminal oxygen atom, and a pair of bridging oxygen atoms. A single metal–metal bond between molybdenum atoms with a typical separation of 2.5–2.6 Å contributes to the cohesion of the unit.[6] Its six sites open for further coordination are not equivalent: the two which are in *trans* positions relative to the terminal oxo groups are subject to their labilizing *trans* influence and consequently bonding of the ligands at these sites is weaker when compared to the four equatorial sites. Various supramolecular complexes, encompassing discrete species[7] and infinite 1D or 2D arrays[8–10] could be prepared by combining the reactive $\{Mo_2O_4\}^{2+}$ precursors and multidentate ligands. Unfortunately, the control over the reaction outcome cannot be gained solely by tuning the ligand-to-molybdenum ratio. When the amount of the ligand was small, a necessary condition for the formation of polymeric phases, the metal centres attained the coordination saturation through the self-assembly of $\{Mo_2O_4\}^{2+}$ cores, enabled by the ability of oxo groups to participate in μ_3- and μ_4-bridging interactions.[7a] The latter process is the reason for the scarcity of polymeric $\{Mo_2O_4\}^{2+}$ complexes with multidentate ligands. The literature reports on only three structurally characterized $\{Mo_2O_4\}^{2+}$ species of this type: an oxalate-bridged $[Mo_2O_4(\mu_2\text{-}C_2O_4)Cl_2]_n^{2n-}$, a phosphate-bridged $[Mo_2O_4(C_2O_4)_2(\mu_2\text{-}H_2PO_4)]_n^{3n-}$, both with an infinite chain structure, and a phosphate-bridged $[Mo_2O_4(PO_4)(HPO_4)]_n^{3n-}$ with an infinite layer structure.[8–10] No preferential binding pattern of multidentate ligands over the six coordination sites of the $\{Mo_2O_4\}^{2+}$ core could be dis-

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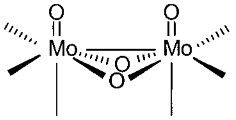
cerned. A normally favoured, chelating coordination of the ligand was observed only in $[Mo_2O_4(\mu_2\text{-}C_2O_4)Cl_2]_n^{2n-}$. We were interested to see how different multidentate ligands, in particular the carboxylate-based ligands with a well-known tendency towards the chelating coordination, coordinate to the $\{Mo_2O_4\}^{2+}$ core. Herein we report the preparation and the structural characterization of a novel anionic tetranuclear heptanedioato complex, $[(Mo_2O_4Cl_4)_2(\mu_4\text{-hda})]^{6-}$, and three 1,3,5-benzenetricarboxylato complexes: anionic dinuclear $[Mo_2O_4X_4(\mu_2\text{-btcH}_2)]^{3-}$ (X = Cl, Br) and a neutral tetranuclear $[(Mo_2O_4Py_3)_2(\mu_3\text{-btcH})_2]$.



Scheme 1. The $\{Mo_2O_4\}^{2+}$ structural core.

Results and Discussion

Solid State Structures

The structures of $(PyH)_4[Mo_2O_4Cl_4(\mu_2\text{-btcH}_2)]Cl$ (**1**) and $(PyH)_4[Mo_2O_4Br_4(\mu_2\text{-btcH}_2)]Br$ (**2**) will be discussed concurrently because of their structural similarity. A dinuclear anion $[Mo_2O_4X_4(\mu_2\text{-btcH}_2)]^{3-}$, depicted in Figure 1a, occu-

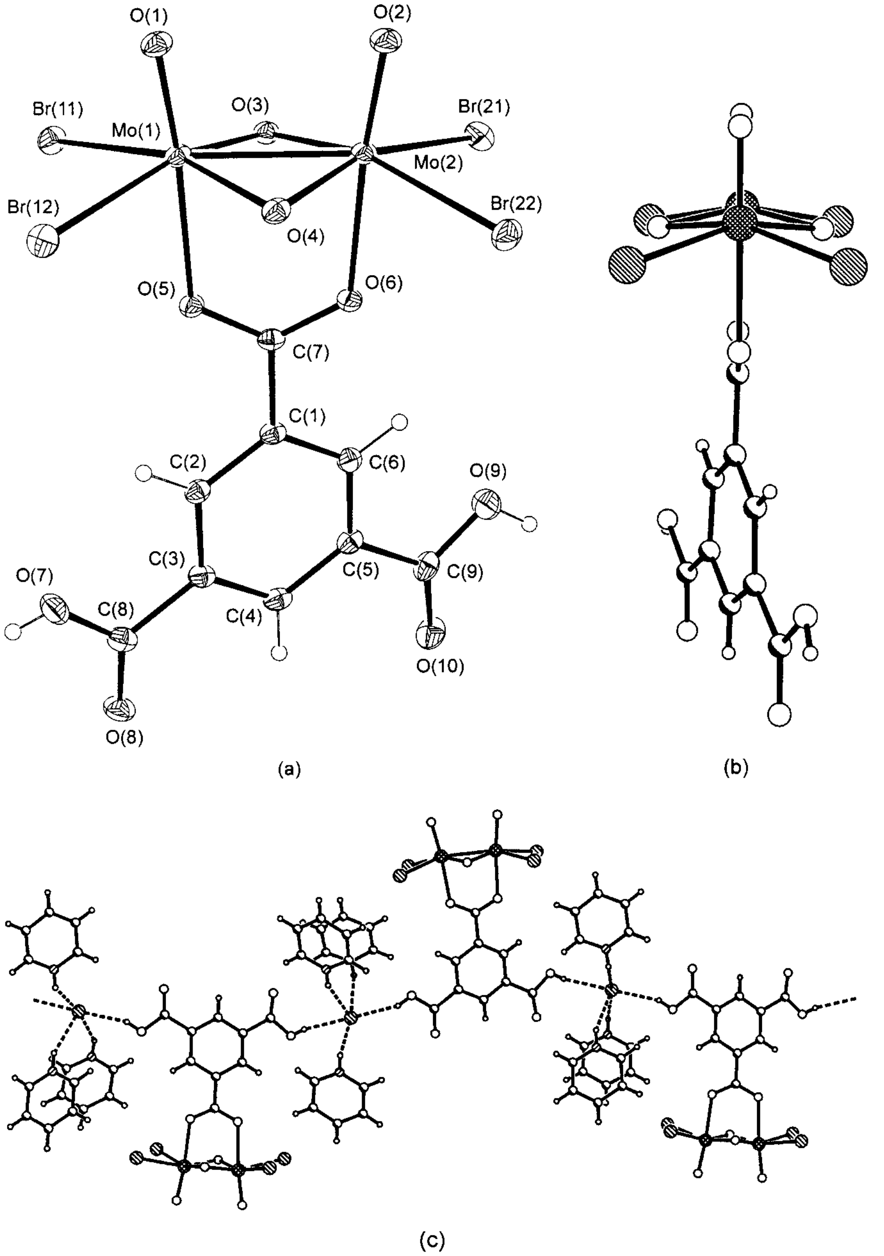


Figure 1. (a) Molecular structure of the anion $[Mo_2O_4Br_4(\mu_2\text{-btcH}_2)]^{3-}$ in **2** with displacement ellipsoids drawn at the 30% probability level. (b) A view along the metal–metal bond vector of the anion in **2** illustrating the orientation of the $btcH_2^-$ ligand. (c) Hydrogen bonds occurring between COOH groups and halide counteranions in **1** and **2** result in infinite chains.

pies a general position within the unit cell of the monoclinic space group $P2_1/n$. Associated with each dinuclear anion are four protonated pyridine molecules and one halide counteranion. Geometric parameters of the basic $\{Mo_2O_4\}^{2+}$ core are very similar to those determined in related compounds:[6] (i) a short distance between molybdenum atoms, 2.5962(4) Å for **1** and 2.5856(3) Å for **2**, typical for a single metal–metal bond; and (ii) a buckled Mo(μ_2-O)$_2$-Mo ring with the metal atoms above and the bridging oxygen atoms below the mean plane. The dihedral angle between the two Mo(μ_2-O)$_2$ planes, 159.85(5)° for **1** and 159.37(4)° for **2**, is greater than the angles observed for $\{Mo_2O_4\}^{2+}$ compounds without the third bridging ligand. A distorted octahedral coordination of each metal centre of the $\{Mo_2O_4\}^{2+}$ core is completed by a pair of halides and an oxygen from the carboxylate group. An exhaustive list of bond lengths is given in Table 1. The carboxylato ligand, the anion of 1,3,5-benzenetricarboxylic acid with two non-ionized carboxylic groups, is coordinated to the metal centres of the $\{Mo_2O_4\}^{2+}$ core, as will be shown presently, in the usual manner, i.e., through both oxygen atoms of the carboxylate group to a pair of molybdenum atoms. This type of carboxylate coordination will be denoted throughout this paper as a *syn-syn* bidentate bridging mode.[11] The carboxylate group thereby serves as a third bridge between a pair of molybdenum atoms. Taking into account that the carboxylate group occupies a pair of *trans* positions relative to Mo=O bonds and is, therefore, subject to their well-documented *trans* influence, the molybdenum-to-carboxylate oxygen bond lengths are relatively short, 2.269(2) and 2.281(2) Å for **1** and 2.270(2) and 2.292(2) Å for **2**. It has been observed that the extent to which the *trans* influence is expressed within a certain species differs from one case to another.[12] Table 2 lists some $\{Mo_2O_4\}^{2+}$ complexes with different carboxylates. In all, the carboxylato ligand occupies a pair of *trans* positions within the $\{Mo_2O_4\}^{2+}$ unit. It can be seen that the Mo–O distances span a wide range and that they can exceed 2.40 Å. The carboxylate group in all listed complexes in Table 2 is invariably almost coplanar with the plane defined by a pair of molybdenyl groups. The same observation pertains to the coordinated carboxylate moiety in the anions of **1** and **2**, whereas the benzene ring of the btcH$_2^-$ ligand with both carboxylic groups is slightly rotated away (Figure 1b). The protonated carboxylate groups and pyridinium cations, which can act as donors of hydrogen bonds, are matched with the halide counteranions and the doubly-bridging oxygen atoms as the acceptors. The hydrogen bonding interactions between the carboxylic groups and halide counteranions result in infinite chains that propagate along the [10–1] unit cell direction (Figure 1c). The corresponding O(7)···X and O(9)···X distances are 2.920(3) and 2.938(3) Å for **1** and 3.084(3) and 3.093(2) Å for **2**. The halide counteranion also forms hydrogen bonds to three protonated pyridine molecules with the N···X distances ranging from 3.112(3) to 3.291(3) Å for **1** and from 3.240(3) to 3.415(3) Å for **2**. Protonated pyridine

Table 1. Selected interatomic distances [Å] for compounds **1** and **2**.[a]

	1	**2**
Mo(1)–Mo(2)	2.5962(4)	2.5856(3)
Mo(1)–O(1)	1.683(2)	1.679(2)
Mo(2)–O(2)	1.681(2)	1.678(2)
Mo(1)–O(3)	1.952(2)	1.952(2)
Mo(1)–O(4)	1.977(2)	1.973(2)
Mo(2)–O(3)	1.952(2)	1.954(2)
Mo(2)–O(4)	1.975(2)	1.970(2)
Mo(1)–X(11)	2.4426(8)	2.5901(3)
Mo(1)–X(12)	2.4695(9)	2.6320(4)
Mo(2)–X(21)	2.4528(8)	2.5994(4)
Mo(2)–X(22)	2.4555(9)	2.6160(4)
Mo(1)–O(5)	2.281(2)	2.292(2)
Mo(2)–O(6)	2.269(2)	2.270(2)
C(7)–O(5)	1.272(4)	1.267(3)
C(7)–O(6)	1.267(4)	1.263(3)
C(8)–O(7)	1.326(4)	1.321(4)
C(8)–O(8)	1.213(4)	1.213(3)
C(9)–O(9)	1.321(4)	1.326(4)
C(9)–O(10)	1.208(4)	1.212(4)

[a] Same labelling scheme pertains to compounds **1** and **2**.

Table 2. Selected geometric parameters [Å, °] for some carboxylate molybdenum(V) complexes with the $\{Mo_2O_4\}^{2+}$ core.

Compound	Mo–Mo	Fold angle[a]	Mo–O(carboxylate)[b]
1	2.5962(4)	159.85(5)	2.269(2), 2.281(2)
2	2.5856(3)	159.37(4)	2.270(2), 2.292(2)
3	2.5410(3)	160.4(1)	2.209(2), 2.343(2)
	2.5326(3)	160.1(1)	2.233(2), 2.325(2)
4	2.5824(3)	159.9(1)	2.274(2), 2.320(2)
$[Mo_2O_4Cl_4(\mu_2\text{-maleH})]^{3-}$ [12][c]	2.5916(3)	156.49(9)	2.380(2), 2.438(2)
	2.5951(3)	158.3(1)	2.371(2), 2.377(2)
$[Mo_2O_4Br_4(\mu_2\text{-maleH})]^{3-}$ [12][c]	2.5724(4)	156.44(6)	2.316(2), 2.413(2)
$[Mo_2O_4(SCN)_4(\mu_2\text{-OOCCH}_3)]^{3-}$ [13][d]	2.560(1)		2.277(7), 2.335(6)
$[Mo_2O_4(\mu_2\text{-OOCH})(OOCH)_4]^{3-}$ [14]	2.5490(5)	162.6	2.302(2)[e]
$[\{Mo_2O_4(mal)_2\}_2(\mu_4\text{-mal})]^{6-}$ [15][f]	2.555	161	2.321[g]

[a] A dihedral angle between the Mo(μ_2-O)$_2$ planes of the $\{Mo_2O_4\}^{2+}$ core. [b] The distance pertains to the carboxylate bonded in the *syn-syn* bidentate bridging manner. [c] maleH = hydrogen maleate ion. [d] Fold angle was not reported. [e] The monodentate terminal formate ions bind to molybdenum with bond lengths of 2.085(2) and 2.130(2) Å. [f] mal = $CH_2(COO)_2^{2-}$. [g] The chelating malonate ions bind to molybdenum with bond lengths of 2.081 Å.

molecules are engaged in another type of interaction. These occur with both doubly bridging oxo groups of the $\{Mo_2O_4\}^{2+}$ core. Their lengths are 2.711(4)–2.802(4) Å for **1** and 2.708(3)–2.844(3) Å for **2**.[16]

The structure of **3** consists of neutral, tetranuclear molecules with the $[(Mo_2O_4Py_3)_2(\mu_3\text{-btcH})_2]$ composition and pyridine solvent molecules. Two $\{Mo_2O_4\}^{2+}$ moieties are linked by two carboxylato ligands to form a tetranuclear molecule (Figure 2a). Both carboxylato ligands, each with a nonionized carboxylic group and two deprotonated ones, are bound in the same way: with one carboxylate group in the usual *syn-syn* bidentate bridging mode to a pair of metal atoms of the $\{Mo_2O_4\}^{2+}$ unit in the asymmetric manner [2.209(2) vs. 2.343(2) and 2.233(2) vs. 2.325(2) Å] and with the other carboxylate group in a monodentate manner to molybdenum from the other dinuclear unit (Figure 2b) with bond lengths of 2.068(2) and 2.070(2) Å. The asymmetric carboxylate coordination finds precedence in several other complexes (see Table 2). No adequate explanation could be provided in either case.[12] The $\{Mo_2O_4\}^{2+}$ core with the *syn-syn* bidentately bridging carboxylato ligand resembles the anions of **1** and **2**. The carboxylate group is coplanar

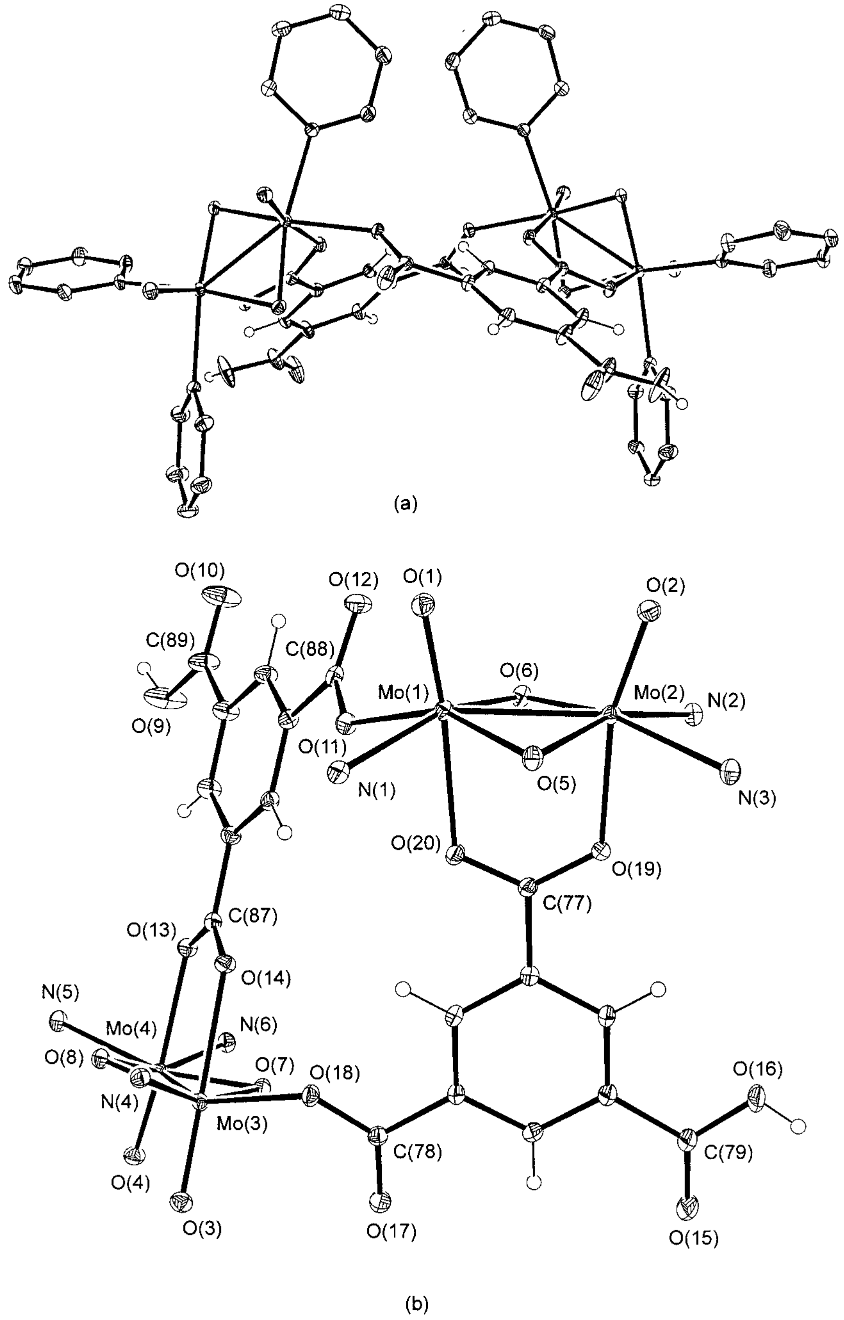


Figure 2. (a) Molecular structure of $[(Mo_2O_4Py_3)_2(\mu_3\text{-btcH})_2]$ in **3** with displacement ellipsoids drawn at the 30% probability level. Pyridine hydrogen atoms have been omitted for clarity. (b) The tetranuclear complex of **3** in a different orientation. Pyridine carbon and hydrogen atoms have been omitted.

with the plane of two molybdenyl groups, while the remaining part of the ligand is rotated away from this plane. The misalignment of the two planes is smaller in complex **3** than in the anions of **1** and **2**, as shown by the values of the corresponding dihedral angles, 5.42(7) and 8.99(7)° for **3** vs. 17.79(6) for **1** and 20.80(5)° for **2**. The participation of btcH^{2-} ligands in **3** in a monodentate coordination via another carboxylate group may well be responsible for such a conformation of the ligand. Each btcH^{2-} ligand thus connects three molybdenum atoms: a pair of metal atoms from one $\{Mo_2O_4\}^{2+}$ unit is connected via a long bridge with molybdenum from another dinuclear unit. The separations between the molybdenum atoms are in the range 8.1894(9)–11.0690(4) Å. The geometric parameters of the $\{Mo_2O_4\}^{2+}$ moieties are: (i) separations between molybdenum atoms of 2.5410(3) and 2.5326(3) Å; and (ii) fold angles of 160.4(1) and 160.1(1)°. A distorted octahedral environment of molybdenum atoms in **3** is completed by pyridine ligands. The rather short length of the metal–metal bonds in **3** may be explained in terms of the high content of pyridine ligands whose nature is electron-donating. As a rule, longer metal–metal bonds occur in complexes with the electron-withdrawing ligands such as chloro or bromo ligands. Although the entire tetranuclear molecule of **3** is the crystallographic asymmetric unit, it comes very close to having C_2 symmetry with the C_2 axis going through the centre of the loop delineated by Mo(1), a btcH^{2-} ligand, Mo(3) and another btcH^{2-} ligand. As far as the bonding pattern in the distorted octahedral environment of each molybdenum atom is concerned, the pairwise equivalences demanded by the C_2 symmetry are very closely approximated. An exhaustive list of bond lengths is given in Table 3. The nonionized carboxylic group of each btcH^{2-} ligand is engaged in hydrogen bonding interaction with a pyridine solvent molecule. The corresponding O···N distances are 2.646(4) and 2.657(4) Å.

Table 3. Selected interatomic distances [Å] for **3**.

Mo(1)–Mo(2)	2.5410(3)	Mo(3)–Mo(4)	2.5326(3)
Mo(1)–O(1)	1.681(2)	Mo(3)–O(3)	1.678(2)
Mo(2)–O(2)	1.689(2)	Mo(4)–O(4)	1.694(2)
Mo(1)–O(5)	1.947(2)	Mo(3)–O(7)	1.927(2)
Mo(1)–O(6)	1.926(2)	Mo(3)–O(8)	1.950(2)
Mo(2)–O(5)	1.930(2)	Mo(4)–O(7)	1.934(2)
Mo(2)–O(6)	1.940(2)	Mo(4)–O(8)	1.930(2)
Mo(1)–N(1)	2.260(2)	Mo(3)–N(4)	2.249(2)
Mo(2)–N(2)	2.235(3)	Mo(4)–N(5)	2.254(2)
Mo(2)–N(3)	2.251(2)	Mo(4)–N(6)	2.233(3)
Mo(1)–O(20)	2.343(2)	Mo(3)–O(14)	2.325(2)
Mo(2)–O(19)	2.209(2)	Mo(4)–O(13)	2.233(2)
Mo(1)–O(11)	2.068(2)	Mo(3)–O(18)	2.070(2)
C(77)–O(19)	1.274(4)	C(87)–O(13)	1.274(4)
C(77)–O(20)	1.258(3)	C(87)–O(14)	1.258(3)
C(78)–O(18)	1.294(3)	C(88)–O(11)	1.300(3)
C(78)–O(17)	1.227(4)	C(88)–O(12)	1.226(4)
C(79)–O(16)	1.320(4)	C(89)–O(9)	1.306(4)
C(79)–O(15)	1.211(4)	C(89)–O(10)	1.209(4)

The ionic structure of **4** consists of tetranuclear anions with the $[(Mo_2O_4Cl_4)_2(\mu_4\text{-hda})]^{6-}$ composition (Figure 3), protonated pyridine molecules as countercations and solvent molecules of acetonitrile. The linkage of two basic $\{Mo_2O_4\}^{2+}$ cores to produce a tetranuclear structure is achieved via a quadridentate hda^{2-} ligand whose two carboxylate groups occupy *trans* positions within both $\{Mo_2O_4\}^{2+}$ cores. Each carboxylate group of the hda^{2-} ligand is coordinated in the *syn-syn* bidentate bridging manner and serves as a third bridge between a pair of metal–metal bonded atoms whose separation, 2.5824(3) Å, falls in the normally observed range. The hda^{2-} ligand thus connects four molybdenum atoms: two pairs are connected via a long bridge consisting of the whole hda^{2-} ligand. The resulting separations between the molybdenum atoms from different dinuclear subunits are in the 8.9043(4)–11.6186(4) Å range. The molybdenum-to-carboxylate bond lengths, subject to the labilizing *trans* influence of the Mo=O bonds, reveal an asymmetric bonding pattern, 2.274(2) vs. 2.320(2) Å. The tetranuclear anion has a twofold rotation symmetry. The anion sits with the central carbon atom of the alkyl chain on a special position within the *C*2/*c* space group, on a twofold rotation axis. The pattern of hydrogen bonds in **4** is typical for anionic $\{Mo_2O_4\}^{2+}$ complexes with protonated pyridine molecules as the countercations: each doubly-bridging oxygen from the $\{Mo_2O_4\}^{2+}$ core is linked to a pyridinium cation. The corresponding N···O distances are 2.710(3) and 2.732(3) Å. The remaining two pyridinium cations participate in another type of hydrogen bonding interaction: each forms a relatively short hydrogen bond with one of the four coordinated chloro ligands, N(2)···Cl(21) = 3.071(3) Å, leading to a nonequivalence of the molybdenum-to-chlorine bond lengths. As expected, the respective bond length is longer than the others. A list of bond lengths is given in Table 4.

In spite of the wide use of 1,3,5-benzenetricarboxylate anions in coordination chemistry, the literature reports on only one molybdenum(v) complex with this ligand, a cyclic $[Mo_{12}S_{12}O_{12}(OH)_{12}(\mu_6\text{-btc})]^{3-}$ anion.[17] The dodecanuclear complex consists of six $\{Mo_2O_2(\mu_2\text{-S})_2\}^{2+}$ moieties arranged around the central btc^{3-} anion which is coordinated with each of its carboxylate groups in the *syn-syn* bidentate bridging manner. The btc^{3-} anion serves on the whole as a μ_6-ligand with the molybdenum-to-carboxylate oxygen bond lengths in the 2.350(10)–2.425(10) Å range. The ability of inorganic rings with the general formula $[Mo_nO_nS_n(OH)_n]$ (n = 8, 10, 12) to encapsulate in their centres organic templates was further exploited in the preparation of $[Mo_{12}S_{12}O_{12}(OH)_{12}(\mu_6\text{-hda})]^{2-}$, the only structurally characterized molybdenum(v) heptanedioato complex prior to this study.[18] Each carboxylate group of the ligand is coordinated to three molybdenum atoms as follows: one oxygen atom is bonded to the metal atom of the $\{Mo_2O_2(\mu_2\text{-S})_2\}^{2+}$ moiety, while the other oxygen binds to the other metal atom of the same dinuclear core and also to molybdenum from the neighbouring dinuclear core. The heptanedioate thus serves as a μ_6-ligand with the molybdenum-to-carboxylate oxygen bond lengths in the 2.341(12)–2.440(9) Å range. Both ring structures are essentially planar. The most apparent difference between them is the shape of

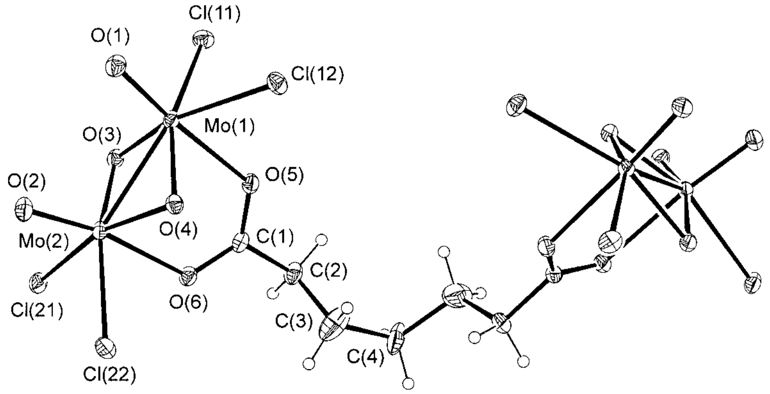


Figure 3. Molecular structure of the anion $[(Mo_2O_4Cl_4)_2(\mu_4\text{-hda})]^{6-}$ in **4** with displacement ellipsoids drawn at the 30% probability level.

Table 4. Selected interatomic distances [Å] for **4**.

Mo(1)–Mo(2)	2.5824(3)
Mo(1)–O(1)	1.682(2)
Mo(2)–O(2)	1.685(2)
Mo(1)–O(3)	1.952(2)
Mo(1)–O(4)	1.959(2)
Mo(2)–O(3)	1.947(2)
Mo(2)–O(4)	1.944(2)
Mo(1)–Cl(11)	2.4467(7)
Mo(1)–Cl(12)	2.4598(6)
Mo(2)–Cl(21)	2.4947(6)
Mo(2)–Cl(22)	2.4840(7)
Mo(1)–O(5)	2.320(2)
Mo(2)–O(6)	2.274(2)
C(1)–O(5)	1.255(3)
C(1)–O(6)	1.275(3)

the ring: a perfect cycle for the btc^{3-} complex and an oval ring for the hda^{2-} complex.

Although the carboxylate group is known to coordinate in several different ways,[11] a survey of molybdenum(v) carboxylate complexes reveals that a number of possible coordination modes reduces to only two: (i) a monodentate terminal mode; and (ii) a *syn-syn* bidentate bridging mode. Speaking in terms of distances, the carboxylato ligand spans in the latter case distances between metal atoms as short as 2.5–2.6 Å and at the other extreme, as long as 3.850 Å as exemplified by $[Mo_4O_6(\mu_2\text{-OOCCH}_3)_6Cl_2]$.[19] It is pertinent to note that in no instance was a chelating coordination of carboxylate encountered among molybdenum(v) complexes. The X-ray structures of two thiobenzoato complexes, $[Mo_2O_2S_2(OSCC_6H_5)_2Py_2]$ and $[Mo_2O_2S_2(OSCC_6H_5)_2(4\text{-MePy})_2]$ (4-MePy = 4-methylpyridine), demonstrate that thio derivatives of carboxylato ligands are capable of chelating coordination.[20] The same binding scheme emerges upon inspection of the rare di- and tricarboxylato molybdenum(v) complexes. In addition to the above-described coordination modes, only two new ones are displayed: (i) the coordination of each carboxylate group of the hda^{2-} ligand to three metal atoms in $[Mo_{12}S_{12}O_{12}(OH)_{12}(\mu_6\text{-hda})]^{2-}$;[18] and (ii) the chelating coordination of malonate ions in $[\{Mo_2O_4(mal)_2\}_2(\mu_4\text{-mal})]^{6-}$ via two oxygen atoms, each belonging to a different carboxylate group.[15] The binding modes adopted by the $btcH_2^{-}$, $btcH^{2-}$, and hda^{2-} ligands in the title complexes add further validity to the observed binding scheme of carboxylato ligands in complexes with molybdenum(v).

In contrast to numerous oligonuclear complexes obtained upon the self-assembly of $\{Mo_2O_4\}^{2+}$ cores,[6] species where two or more dinuclear subunits are linked covalently solely by multidentate ligands are extremely rare. Apart from the three polymeric species, already mentioned in the introduction, that leaves to the best of our knowledge two tetranuclear anions, $[\{Mo_2O_4(\eta^2\text{-}C_2O_4)_2\}_2(\mu_4\text{-}C_2O_4)]^{6-}$[21] and $[\{Mo_2O_4(mal)_2\}_2(\mu_4\text{-mal})]^{6-}$,[15] where the linkage is achieved via quadridentate oxalate and malonate, respectively. Their structural analogy to $[(Mo_2O_4Cl_4)_2(\mu_4\text{-hda})]^{6-}$, the anion in **4**, is obvious: pairs of dinuclear subunits are linked covalently by dicarboxylates, differing in the number of carbon atoms between the carboxylate groups. It is to be noted that a class of related $\{Mo_2O_2(\mu_2\text{-S})_2\}^{2+}$ species also reveals tetranuclear anions of this type, $[\{Mo_2O_2S_2(\eta^2\text{-}C_2O_4)_2\}_2(\mu_4\text{-}C_2O_4)]^{6-}$[22] and $[\{Mo_2O_2S_2(\eta^2\text{-SO}_4)_2\}_2(\mu_4\text{-SO}_4)]^{6-}$.[23] The X-ray structure analysis of $[\{Mo_2O_4(\eta^2\text{-}$

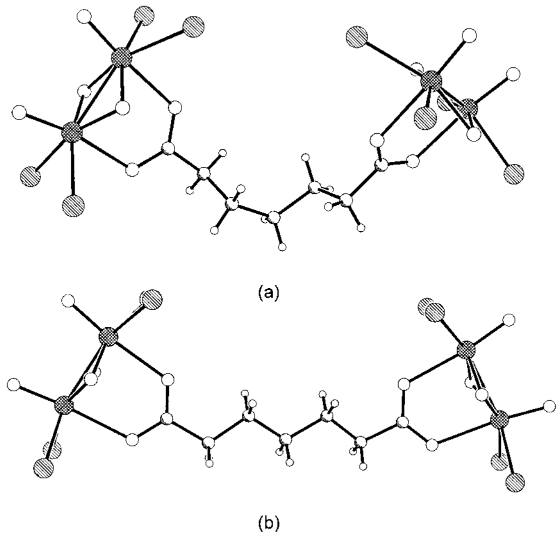


Figure 4. Two different conformations of the $[(Mo_2O_4Cl_4)_2(\mu_4\text{-hda})]^{6-}$ anion as found in **4** (a) and **5** (b).

$C_2O_4)_2\}_2(\mu_4\text{-}C_2O_4)]^{6-}$ revealed the μ_4-oxalate in a complete staggered conformation, whereas the μ_4-oxalate in $[\{Mo_2O_2S_2(\eta^2\text{-}C_2O_4)_2\}_2(\mu_4\text{-}C_2O_4)]^{6-}$ adopted the usual planar form. With dicarboxylates that contain alkyl chains, the existence of complexes with different chain conformations in the solid state seems very likely. The $[(Mo_2O_4Cl_4)_2(\mu_4\text{-hda})]^{6-}$ anion, found in **4** and **5**, presents such a case. The alkyl chain in the anion of **5** is straighter than in **4** (Figure 4). Consequently, the separations between molybdenum atoms from the two $\{Mo_2O_4\}^{2+}$ moieties in **5** are larger than in **4**. The $[(Mo_2O_4Cl_4)_2(\mu_4\text{-hda})]^{6-}$ anions in **4** and **5** also differ in the mutual orientations of the metal–metal bond vectors. Unfortunately, the low-quality X-ray data of **5** does not allow any further discussion of its structural parameters. The linkage of two dinuclear subunits with the agency of $btcH^{2-}$ ligands in $[(Mo_2O_4Py_3)_2(\mu_3\text{-}btcH)_2]$ (**3**) finds no precedence.

Infrared Spectroscopy

The positions of asymmetric and symmetric ν(COO) vibrations can be used to diagnose the carboxylate binding mode: large Δ values, defined as $\nu_{asym}(COO) - \nu_{sym}(COO)$, are observed for the monodentate binding mode, while *syn-syn* bidentate bridging carboxylates display Δ values which are close to those observed for ionic compounds.[24] Accordingly, the bands at 1538 and 1410 cm^{-1} in the spectrum of **4** can be attributed to $\nu_{asym}(COO)$ and $\nu_{sym}(COO)$, respectively. The calculated Δ value, 128 cm^{-1}, is in line with the *syn-syn* bidentate bridging coordination. With at least two carboxylate groups of the 1,3,5-benzenetricarboxylate anions in **1**, **2**, and **3** engaged in different binding modes, no unambiguous assignations can be made. The spectra of **1** and **2** are very similar to each other. An absorption band at 1718 cm^{-1} for **1** and bands at 1722 and 1708 cm^{-1} for **2** are indicative of nonionized carboxylic groups in the $btcH_2^-$ ligand. The region of asymmetric and symmetric ν(COO) vibrations displays a number of strong bands, at 1618, 1554, 1539, 1433, and 1365 cm^{-1} for **1** and at 1617, 1537, 1435, and 1365 cm^{-1} for **2**. The spectrum of **3**, with all carboxylate groups distinctly different, displays a band at 1711 cm^{-1} which is associated with the C=O stretching vibration of the carboxylic group and several bands in the region of asymmetric [at 1649, 1607, and 1545 cm^{-1}] and symmetric ν(COO) vibrations [at 1449 and 1406 cm^{-1}]. For comparison, several bands were also observed for $[Cd_{1.5}(btc)(bpe)(H_2O)_2]\cdot H_2O$ [bpe = 1,2-bis(4-pyridyl)ethane] where two carboxylate groups are bound in a chelating manner and the third one is bound monodentately.[3d] Δ values of 122 and 255 cm^{-1} were calculated from their positions.

Synthetic Considerations

The composition of the heptanedioato complex $[(Mo_2O_4Cl_4)_2(\mu_4\text{-hda})]^{6-}$, the anion in **4** and **5**, is as anticipated. Acetonitrile was used as a solvent for its low coordinating ability towards molybdenum(V) and since both, the molybdenum(V) starting material and the tetrabutylammonium heptanedioate, display a good acetonitrile solubility. The substitution of the labile aqua and halo ligands in acetonitrile usually does not proceed beyond the formation of the $\{Mo_2O_4\}^{2+}$ core and so species with a high content of unsubstituted halo ligands can be isolated.[12] The carboxylate groups of the heptanedioate coordinated to two $\{Mo_2O_4\}^{2+}$ cores, resulting in a tetranuclear anion $[(Mo_2O_4Cl_4)_2(\mu_4\text{-hda})]^{6-}$. The successful isolation of $(PyH)_6[(Mo_2O_4Cl_4)_2(\mu_4\text{-hda})]\cdot 2CH_3CN$ (**4**) required a substantial reduction of the volume of the reaction mixture. When too much solvent was removed, a product with a different composition, $(PyH)_{10}[(Mo_2O_4Cl_4)_2(\mu_4\text{-hda})][MoOCl_5]Cl_2$ (**5**), crystallized from the concentrate. The composition of **5** is intriguing for two reasons. Although a sufficient amount of the hda^{2-} ligand was used, its coordination to molybdenum(V) was not quantitative. The identity of the uncomplexed species turned out to be $[MoOCl_5]^{2-}$, giving evidence for the transformation of $[MoOCl_4(H_2O)]^-$ into $[MoOCl_5]^{2-}$.

The compositions of the 1,3,5-benzenetricarboxylato complexes, the $[Mo_2O_4X_4(\mu_2\text{-}btcH_2)]^{3-}$ anions, and the neutral $[(Mo_2O_4Py_3)_2(\mu_3\text{-}btcH)_2]$, didn't meet expectations. Although fully neutralized salt of 1,3,5-benzenetricarboxylic acid was used in the case of **1** and **2**, the protonation of two carboxylate groups by pyridinium cations, introduced into the reaction mixture via the molybdenum(V) starting materials, prevented their ligation to two more $\{Mo_2O_4\}^{2+}$ units. The only carboxylate group of the 1,3,5-benzentricarboxylate capable of coordination attached to the $\{Mo_2O_4\}^{2+}$ core in the usual manner. Because of the greater lability of bromo vs. chloro ligands, the crystallization of **2** was not as straightforward as that of **1**, it took longer and the yield was significantly smaller. An important role for the solvent was observed. When methanol or ethanol was used in place of acetonitrile, the coordination of alcohol and alkoxide to the $\{Mo_2O_4\}^{2+}$ core took place first, followed by the assembly of two $\{Mo_2O_4\}^{2+}$ units into a tetranuclear $\{Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OR)_2\}^{2+}$ core. The composition of the final products as $(PyH)_2[Mo_4O_8(OR)_2(ROH)_2X_4]$ (R = Me, Et; X = Cl, Br) was established on the basis of their infrared spectra.[25–26] Carrying out the reaction between $(PyH)[MoOBr_4]$ and 1,3,5-benzenetricarboxylic acid in pyridine, a solvent with a strong coordinating ability, at 115 °C resulted in the coordination of both ligands and a neutral complex $[(Mo_2O_4Py_3)_2(\mu_3\text{-}btcH)_2]$ (**3**) was isolated. By using the oxobromomolybdate(V) starting material, the number of labile sites in the molybdenum(V) coordination sphere was increased. The $btcH^{2-}$ ligand with two carboxylate groups is capable of coordination to two $\{Mo_2O_4\}^{2+}$ cores, yet in $[(Mo_2O_4Py_3)_2(\mu_3\text{-}btcH)_2]$ (**3**) the coordination of both in the *syn-syn* bidentate bridging manner was not realized. Namely, one carboxylate group coordinated monodentately. The large amount of the ligand used explains the formation of a discrete species.

Conclusions

A series of 1,3,5-benzenetricarboxylato and heptanedioato molybdenum(V) complexes based on the $\{Mo_2O_4\}^{2+}$

structural core was prepared. The carboxylate group usually binds to a pair of metal atoms of the $\{Mo_2O_4\}^{2+}$ core in the *syn-syn* bidentate bridging manner. Coordination of two carboxylate groups of either 1,3,5-benzenetricarboxylate or heptanedioate results in the formation of tetranuclear clusters.

Experimental Section

General Remarks: All manipulations and procedures were conducted in air. Chemicals were purchased from Aldrich and used as received. $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ and $(PyH)[MoOBr_4]$ were prepared as reported.[26–27] The solvothermal reactions were carried out in sealed glass tubes under autogenous pressure. 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.

Preparation of the Acetonitrile Solution of $(n\mathrm{Bu}_4\mathrm{N})_3$btc: 1,3,5-benzenetricarboxylic acid (2.1 g, 0.010 mol) was dissolved in methanol (35 mL), followed by the addition of a methanol solution (1.0 M) of $n\mathrm{Bu}_4\mathrm{NOH}$ (30 mL, 0.030 mol). Methanol was removed by careful pumping on the vacuum line. Acetonitrile was added (20 mL) to the oily residue. Each gram of the resulting solution contained 0.315 mmol of $(n\mathrm{Bu}_4\mathrm{N})_3$btc.

Preparation of the Acetonitrile Solution of $(n\mathrm{Bu}_4\mathrm{N})_2$hda: Heptanedioic acid ($w$ = 0.98, 1.429 g, 8.74 mmol) was dissolved in methanol (10 mL) followed by the addition of a methanol solution (1.0 M) of $n\mathrm{Bu}_4\mathrm{NOH}$ (17.5 mL, 17.5 mmol). Methanol was removed by careful pumping on the vacuum line. Acetonitrile (30 mL) was added to the oily residue. Each gram of the resulting solution contained 0.355 mmol of $(n\mathrm{Bu}_4\mathrm{N})_2$hda.

$(PyH)_4[Mo_2O_4Cl_4(\mu_2\text{-}btcH_2)]Cl$ (1): $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ (450 mg, 1.05 mmol of Mo) was dissolved in acetonitrile (20 mL). A weighted amount of the acetonitrile solution of $(n\mathrm{Bu}_4\mathrm{N})_3$btc (0.647 mmol) was added dropwise with constant stirring. The reaction mixture was left to stand at 8 °C in the refrigerator. The orange, block-shaped crystals of **1** that formed after three days were collected by filtration and washed with the hexanes. Yield: 53% (269 mg). $C_{29}H_{29}Cl_5Mo_2N_4O_{10}$ (962.7): calcd. C 36.18, H 3.04, N 5.82; found C 36.44, H 3.27, N 6.11. IR: $\tilde{\nu}$ = 3228 (w), 3156 (w), 3134 (w), 3090 (w), 3059 (w), 1718 (vvs), 1635 (s), 1618 (vs), 1554 (s), 1539 (vs), 1488 (vvs), 1458 (w), 1433 (vs), 1365 (vs), 1245 (m), 1201 (s), 1183 (vvs), 1163 (vs), 1108 (w), 1097 (w), 1048 (w), 1000 (w), 957 (vvs), 940 (s), 893 (w), 766 (s), 750 (vvs), 694 (m), 678 (vs), 665 (vvs), 649 (vvs), 606 (vvs), 513 (s), 488 (s), 428 (m), 397 (m), 384 (s), 373 (vs), 330 (vvs), 310 (s), 299 (vvs), 292 (vvs), 272 (vs) cm^{-1}.

$(PyH)_4[Mo_2O_4Br_4(\mu_2\text{-}btcH_2)]Br$ (2): $(PyH)[MoOBr_4]$ (540 mg, 1.06 mmol) was dissolved in acetonitrile (20 mL). A weighted amount of the acetonitrile solution of $(n\mathrm{Bu}_4\mathrm{N})_3$btc (0.647 mmol) was added dropwise with constant stirring. The volume of the reaction mixture was reduced on the following day to ca. one half by pumping on the vacuum line. The solution was allowed to stand at ambient conditions. The orange, block-shaped crystals of **2** which formed after six days were collected by filtration and washed with the hexanes. Yield: 19% (119 mg). $C_{29}H_{29}Br_5Mo_2N_4O_{10}$ (1185.0): calcd. C 29.40, H 2.47, N 4.73; found C 29.23, H 2.52, N 4.70. IR: $\tilde{\nu}$ = 3219 (w), 3132 (w), 3057 (w), 1722 (vvs), 1708 (s), 1636 (m), 1617 (s), 1537 (s), 1487 (vvs), 1435 (s), 1365 (s), 1246 (w), 1201 (w), 1173 (vs), 1162 (vs), 1107 (w), 1058 (w), 1049 (w), 1026 (w), 1001 (w), 958 (vvs), 941 (s), 893 (w), 748 (vvs), 721 (w), 697 (m), 677 (vvs), 664 (vs), 635 (w), 605 (s), 510 (m), 477 (m), 424 (w), 397 (w), 379 (m), 357 (s), 325 (m), 264 (m), 252 (m) cm^{-1}.

$[(Mo_2O_4Py_3)_2(\mu_3\text{-}btcH)_2]\cdot 6Py$ (3): A glass tube was charged with $(PyH)[MoOBr_4]$ (120 mg, 0.235 mmol), 1,3,5-benzenetricarboxylic acid (220 mg, 1.05 mmol) and pyridine (4 mL). The tube was sealed and heated for 90 h in an electric oven maintained at 115 °C. After cooling to room temperature, the reaction mixture consisted of a clear, orange solution and colourless, crystalline material. Red, block-shaped crystals of **3** which formed after one month were separated manually from the colourless phase. Yield: 55% (61 mg). Note: The crystals lost interstitial solvent and turned powdery immediately upon removal from the mother liquor. IR: $\tilde{\nu}$ = 3112 (w), 3078 (w), 1958 (w), 1711 (m), 1649 (vs), 1633 (m), 1607 (vs), 1573 (w), 1545 (s), 1486 (m), 1449 (vs), 1436 (m), 1406 (m), 1319 (s), 1291 (s), 1271 (vs), 1234 (m), 1218 (vs), 1161 (m), 1102 (w), 1071 (s), 1046 (s), 1016 (m), 1007 (m), 966 (vvs), 942 (vs), 758 (vvs), 742 (vvs), 718 (vs), 694 (s), 641 (m), 626 (m), 570 (s), 524 (w), 474 (w), 452 (m), 436 (m), 410 (w), 371 (m), 317 (s), 277 (s), 256 (w) cm^{-1}.

$(PyH)_6[(Mo_2O_4Cl_4)_2(\mu_4\text{-}hda)]\cdot 2CH_3CN$ (4): $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ (450 mg, 1.05 mmol of Mo) was dissolved in acetonitrile (20 mL). A weighted amount of the acetonitrile solution of $(n\mathrm{Bu}_4\mathrm{N})_2$hda (0.65 mmol) was added dropwise with constant stirring. The solution was concentrated on the following day on the vacuum line to ca. one half of the initial volume. The resulting solution was left to stand at ambient conditions overnight. The yellow, plate-shaped crystals of **4** were collected by filtration and washed with the hexanes. Yield: 26% (105 mg). $C_{41}H_{52}Cl_8Mo_4N_8O_{12}$ (1516.3): calcd. C 32.48, H 3.46, N 7.39; found C 32.42, H 3.53, N 7.12. IR: $\tilde{\nu}$ = 3223 (w), 3160 (w), 3130 (w), 2249 (m), 1634 (m), 1612 (s), 1538 (vvs), 1486 (vvs), 1410 (vs), 1273 (w), 1250 (m), 1202 (m), 1163 (m), 1048 (m), 1024 (m), 1002 (m), 960 (vvs), 938 (vvs), 879 (w), 758 (vvs), 740 (vvs), 708 (vvs), 682 (vvs), 663 (w), 639 (w), 604 (s), 517 (m), 483 (m), 448 (w), 398 (w), 379 (s), 292 (vvs), 262 (vs) cm^{-1}.

$(PyH)_{10}[(Mo_2O_4Cl_4)_2(\mu_4\text{-}hda)][MoOCl_5]Cl_2$ (5): The same procedure was used as for **4**, only the initial solution was concentrated to ca. 2 mL and left to stand at ambient conditions. Large, yellow-orange, block-like crystals of **5** deposited from the solution overnight. Yield: 11% (51 mg). ***Note:*** The crystals decompose in air.

X-ray Crystallographic Study: 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. Data reduction and integration were performed with the software package DENZO-SMN.[28] Averaging of the symmetry-equivalent reflections largely compensated for the absorption effects. For all compounds, the coordinates of some or all of the non-hydrogen atoms were found via direct methods using the structure solution program SHELXS.[29] The positions of the remaining non-hydrogen atoms were located by use of a combination of least-squares refinement and difference Fourier maps in the SHELXL-97 program. The carboxylic hydrogen atoms in **1** and **2**, located in the final stages of refinement from the difference Fourier maps, were refined with isotropic displacement parameters. The remaining hydrogen atoms were added in calculated positions. Although the R_1 and wR_2 residuals for the least-squares refinement of **5** are large (R_1 almost 10%), its composition, determined to be $(PyH)_{10}[(Mo_2O_4Cl_4)_2(\mu_4\text{-}hda)][MoOCl_5]Cl_2$, is unquestionable. Unfortunately, repeated attempts to obtain crystals with better diffraction data have not been successful. Therefore, we only report some basic crystal data (triclinic, space group $P1$, a = 9.9381(2), b = 14.3948(2), c = 15.5022(3) Å, α = 69.9388(8), β = 86.5969(7), γ = 89.1332(7)°, V = 2079.44(6) Å^3, Z = 1, T = 150(2) K, 29834 mea-

Table 5. Crystallographic data for compounds **1**, **2**, **3**, and **4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{29}H_{29}Cl_5Mo_2N_4O_{10}$	$C_{29}H_{29}Br_5Mo_2N_4O_{10}$	$C_{78}H_{68}Mo_4N_{12}O_{20}$	$C_{41}H_{52}Cl_8Mo_4N_8O_{12}$
Formula mass	962.69	1184.99	1877.20	1516.27
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$Pcab$	$C2/c$
T [K]	150(2)	150(2)	150(2)	150(2)
a [Å]	15.0672(2)	14.9928(1)	17.8525(1)	35.2318(3)
b [Å]	14.0299(2)	14.1363(1)	29.1533(2)	9.2980(1)
c [Å]	17.3771(3)	18.1821(2)	29.9545(2)	20.9025(2)
α [°]	90	90	90	90
β [°]	99.5378(5)	98.5988(4)	90	126.0046(5)
γ [°]	90	90	90	90
V [Å^3]	3622.59(9)	3810.25(6)	15590.1(2)	5539.30(9)
Z	4	4	8	4
λ [Å]	0.71073	0.71073	0.71073	0.71073
μ [mm^{-1}]	1.120	5.958	0.709	1.334
Collected reflections	16036	16750	29052	11882
Unique reflections, R_{int}	8240, 0.0194	8696, 0.0167	15213, 0.0187	6291, 0.0160
Observed reflections	6730	7470	12384	5700
R_1 [$I > 2\sigma(I)$]	0.0359	0.0265	0.0362	0.0267
wR_2 [all data]	0.0966	0.0641	0.1192	0.0826

sured reflections, 16997 unique (R_{int} = 0.056), R_1 [$I > 2\sigma(I)$] = 0.0987 and wR_2 [all data] = 0.2826) and the most relevant geometric parameters of the $[(Mo_2O_4Cl_4)_2(\mu_4\text{-hda})]^{6-}$ anion [Mo–Mo = 2.572(2) and 2.578(2) Å, Mo–Cl = 2.444(5)–2.483(4) Å, Mo–O(hda^{2-} ligand) = 2.291(10)–2.389(10) Å, Mo···Mo (from different $\{Mo_2O_4\}^{2+}$ moieties) = 11.538(2)–14.098(2) Å] and of the $[MoOCl_5]^{2-}$ anion [Mo–O = 1.685(13), Mo–Cl = 2.368(5)–2.533(4) Å]. All the calculations were performed using the WinGX System Version 1.64.05.[30] Figures depicting the structures were prepared using ORTEP3[31] and SHELXTL.[32] Cell parameters and refinement results are summarized in Table 5.

CCDC-271782 (for **1**), -271783 (for **2**), -271784 (for **3**), -271785 (for **4**), and -276050 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information (see also footnote on the first page of this article): Contains infrared spectra of compounds **1**–**4** (Figures S1–S12).

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