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TESI DI LAUREA

Synthesis and Characterization of Molybdenum(VI) Complexes with α-Amino Acids

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Acronyms

aaH = generic α-amino acid with a non polar side-chain in the zwitterionic form. Chirality is omitted (generally referred to the L-enantiomer; to the D- or DL- if specified in the text)

AlaH = L-alanine

GlyH = Glycine

LeuH = L-Leucine

MetH = L-Methionine

(NMe_2)PheH = *N,N*-Dimethyl-L-phenylalanine

PheH = L-Phenylalanine

ProH = L-Proline

SerH = L-Serine

ValH = L-Valine

aaH_2 = generic α-amino acid with a polar side-chain in the zwitterionic form. Chirality is omitted (generally referred to the L-enantiomer; to the D- or DL- if specified in the text)

$AspH_2$ = L-Aspartic acid

$CysH_2$ = L-Cysteine

$GluH_2$ = L-Glutamic acid

$HisH_2$ = L-Histidine

$LysH_2$ = L-Lysine

$TyrH_2$ = L-Tyrosine

acac = Acetylacetonate anion

bipy = 2,2'-Bipyridine

$CitH_4$ = Citric acid

Cp = Cyclopentadienyl anion

CP-MAS = Cross Polarization - Magic Angle Spinning

Cy = Cyclohexene

CyO = Cyclohexene oxide (1,2-Epoxycyclohexane)

$Cy(OH)_2$ = 1,2-Cyclohexanediol

Cy(OH)(OR) = 2-Alkoxycyclohexanol

Cy(−H)OH = 2-Cyclohexenol

Cy(−2H)O = 2-Cyclohexenone

DFT = Discrete Fourier Transform

dien = Diethylenetriamine

DMF = *N,N*-Dimethylformamide

DMSO = Dimethylsulphoxide

EDTA = Ethylenediaminetetraacetate anion

Et = Ethyl

en = Ethylendiamine

FID = Flame Ionization Detector

GC = Gas Chromatography

Gly-Gly-Gly = Glycylglycylglycine

h = Hours

HCBD = Hexachlorobutadiene

HMPT = Hexamethylphosphoramide

PzPy = Pyrazolylpyridine

^{i}Pr = Isopropyl

IR = (Fourier Transform) Infrared (spectroscopy)

M/L = Metal-to-ligand molar ratio

Me = Methyl

min = Minutes

$[Mo]_0$ = Initial molar concentration of molybdenum in the reaction mixture

MS = Mass Spectrometry

^{n}Bu = Butyl (linear)

n.r. = Not Reported

NMR = Nuclear Magnetic Resonance (spectroscopy)

NTA = Nitrilotriacetate anion

RT = Room Temperature

Ph = Phenyl

PicH = Pyridine-2-carboxylic acid (picolinic acid)

P_{OW} = *n*-octanol/water partition ratio

Py = Pyridine

^{t}Bu = *tert*-Butyl

TBHP = *tert*-Butyl hydroperoxide

THF = Tetrahydrofuran

TMS = Tetramethylsilane

UV-Vis = Ultraviolet-Visible (spectroscopy)

Abstract

Molybdenum(VI) complexes of general formula $[Mo_2O_4(OH)_2(\mu\text{-}OH)_2(\mu\text{-}aaH\text{-}\kappa O,\kappa O')]$ have been obtained in high yields by the reaction of the L-enantiopure α-amino acid (aaH = L-phenylalanine, L-leucine, L-methionine, L-proline, *N,N*-dimethyl-L-phenylalanine or glycine) with molybdates ($Na_2MoO_4\cdot2H_2O$, $(NH_4)_2MoO_4$ and $(NH_4)_6Mo_7O_{24}\cdot4H_2O$) in acidic aqueous solution.

The influence on the formation of these complexes of various experimental parameters (pH of the solution, metal-to-ligand molar ratio, concentration and temperature) has been investigated.

Compounds $[Mo_2O_4(OH)_4(aaH)]$ have been characterized by spectroscopic and analytical methods. IR and NMR spectra are consistent for a dinuclear species with *cis*-MoO_2 groups and a zwitterionic amino acid involved in a bidentate bridging coordination through its carboxylate group. A dihydroxo-bridged dinuclear structure and, possibly, a polynuclear oxo-bridged structure, derived from the latter, have been proposed on the basis of DFT calculations. The polymeric nature of these complexes may explain their insolubility in water and in common organic solvents.

The catalytic activity of $[Mo_2O_4(OH)_4(aaH)]$ complexes towards the oxidation of cyclohexene with hydrogen peroxide has been investigated. Catalytic reactions were carried out in acetonitrile, at 65 °C for 3 hours. 1,2-Cyclohexanediols have been obtained as major products, with a good selectivity for the *trans*- diastereomer.

CHAPTER 1

Introduction

Molybdenum is a versatile transition element due to the fact that it possesses a large number of stable and accessible oxidation states.[1] The most stable oxidation state in aqueous solution is molybdenum(VI).[2]

Higher oxidation states of molybdenum, Mo(VI) and Mo(V), are characterized by a strong association with oxygen. This is apparent from the rich and complex chemistry in aqueous solution and from the large number of complexes containing at least one terminal oxo ligand that have been isolated.[3] Most of these complexes are labile, easily reduced and the tendency to form oxo-bridged polynuclear complexes is high.[3] These properties make molybdenum a versatile site for reactions but they also make the clear cut definition of the species present in aqueous solution a challenging experimental problem.[4]

Molybdenum is the only element from the second transition series that occurs in the biological system.[5] The colourless, tetrahedral molybdate ion, $[MoO_4]^{2-}$, lies at the epicentre of high-valent molybdenum chemistry and biochemistry, being an important starting material and the principal bio-available form of molybdenum.[6] Molybdate's size and shape, as well as its ability to participate in strong hydrogen bonding, are essential to its selective binding and transport by proteins.
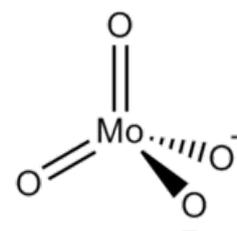
Fig. 1. Structure of the $[MoO_4]^{2-}$ anion

Another important role of molybdenum in living organisms is at the active site of many enzymes involved in oxygen atom transfer reactions[7,8] such as nitrate reductase, xanthine oxidase, sulfite oxidase and aldehyde oxidase.[9] It is believed that, in the catalytic cycle of these enzymes, molybdenum undergoes oxidation state changes between Mo(IV), Mo(V) and Mo(VI), without an increase in nuclearity.

The coordination chemistry of Mo(VI) has aroused a considerable interest in view of its biochemical significance.[10] The chemical information gained in studying molybdenum coordination complexes may be transferable to enzyme structure / function questions not readily solvable by studying the enzymes themselves. For example, dioxomolybdenum(VI) complexes are studied as models for the oxidized forms of molybdoenzymes, which are supposed to contain *cis*-MoX$_2$ units (X = O, S) coordinated to sulphur, nitrogen and oxygen donor atoms of the protein structure.[5,11]
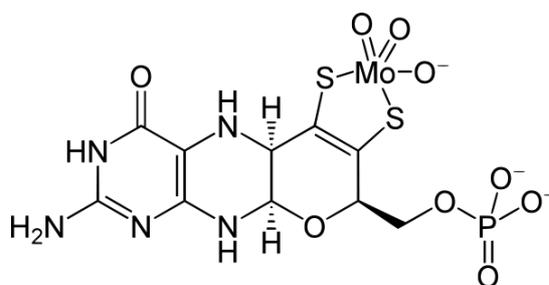
Fig. 2. The *Molybdenum cofactor*, which is required for the activity of enzymes such as sulfite oxidase, xanthine oxidase and aldehyde oxidase, is a dioxomolybdenum(VI) complex [12]

Molybdenum(VI) compounds are used in many catalytic reactions. Several industrial processes such as the ammoxidation of propene to acrylonitrile,[13] olefin epoxidation[14] and olefin metathesis[15] are carried out over molybdenum catalysts. The useful role of molybdenum is not restricted to industrial type catalytic reactions: oxomolybdenum(VI) complexes are widely cited in the literature as catalysts for the oxidation of olefins, alcohols, alkanes, sulphides and amines.[16] The common feature associated with both industrial and biological reactions is that molybdenum serves as the site for a catalytic redox reaction.[17]

Section 1.1 - The aqueous chemistry of molybdenum(VI) - a brief summary

The simplest molybdate is the discrete tetrahedral $[MoO_4]^{2-}$, commercially available as the disodium salt,[1] but also crystallized as dipotassium[18] or diammonium[19] salts.

The multiple, simultaneous protonation equilibria of $[MoO_4]^{2-}$ have been extensively studied.[20] The dianion is stable and inert at pH > 6 but is readily protonated upon acidification (1).[21] The first protonation generates $[HMoO_4]^-$ while the second is accompanied by an increase in coordination number and yields a hexacoordinated neutral species described as $MoO_3(OH)_3$, $MoO_2(OH)_2(H_2O)_2$ or simply $Mo(OH)_6$.[22]

$$[MoO_4]^{2-} \xrightleftharpoons{H^+} [HMoO_4]^- \xrightleftharpoons{H^+, H_2O} [MoO_3(H_2O)_3] \qquad (1)$$
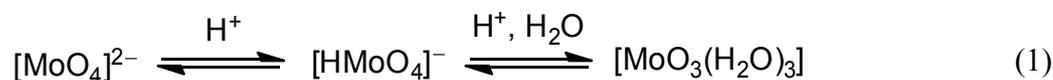
Equilibria between monomeric species are only relevant for very low molybdenum concentrations (< 10^{-4} M). In more concentrated solutions, condensations of $[MoO_4]^{2-}$ leading to polyoxomolybdates occur. Polyoxomolybdates are colourless polynuclear anions formed by edge, corner and (occasionally) face sharing of MoO_6 octahedra[23] and may be represented with the general formula $[H_xMo_yO_z]^{(2z-6y-x)-}$.
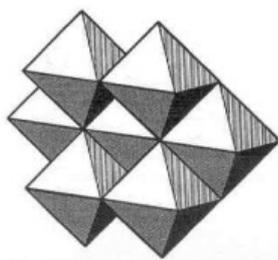
Fig. 3. The structure of $[Mo_7O_{24}]^{6-}$ represented as seven edge sharing MoO_6 octahedra[24]

Polynuclear species play a dominant role from pH = 7 down to 2[25] and have been extensively investigated although it is often difficult to explain why, under given circumstances, a particular degree of aggregation or a particular structure is preferred to other possibilities. The heptamolybdate ion, $[Mo_7O_{24}]^{6-}$ (see figure 3), is the predominant species in solutions with [Mo] > 10^{-3} and pH in the range 3.0-5.5. A commercially available product containing this isopolyanion is ammonium heptamolybdate, $(NH_4)_6[Mo_7O_{24}] \cdot 4H_2O$.
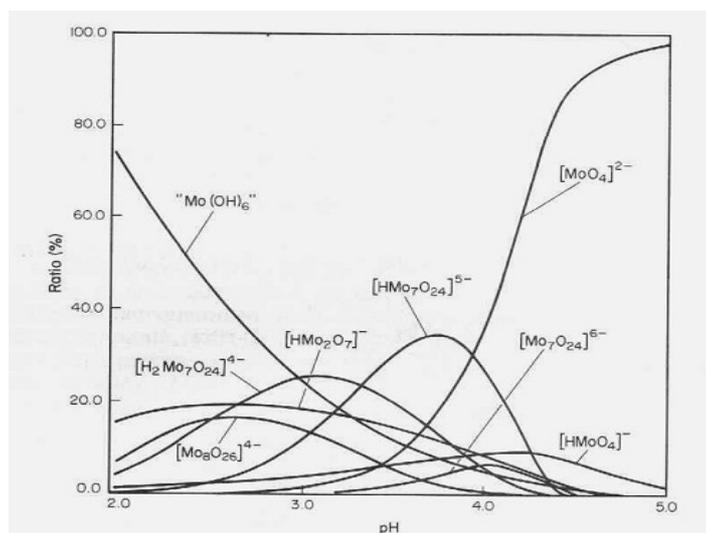

Fig. 4. The distribution of Mo(VI) species with pH for a solution of $5 \cdot 10^{-4}$ M in molybdate at 25 °C, I = 1.0 M (NaCl)[26]

From pH = 2 to pH = 1, depending on the concentration, the break down of polyanions to give the neutral mononuclear $Mo(OH)_6$ occurs. The protonation of $Mo(OH)_6$ to form $[MoO_2(OH)(OH_2)_3]^+$ starts at pH = 2.5 and is complete at an acid concentration of about 1 M.[27,28] At higher acid concentrations, the doubly charged cation $[MoO_2]^{2+}$ starts to form and a formula that has been suggested for this species is cis-$[MoO_2(OH_2)_4]^{2+}$.[29] In 5-12 M hydrochloric acid solution, $[MoO_2Cl_2(H_2O)_2]$ and $[MoO_2Cl_4]^{2-}$ have been observed.[30]

In highly concentrated solutions of nitric[31] or perchloric acid,[32] the precipitation of yellow "molybdic acid" ($MoO_3 \cdot 2H_2O$) is observed, which converts to the monohydrate (indicated as H_2MoO_4 or $MoO_3 \cdot H_2O$) if warmed.[32] The trioxide (MoO_3) can be obtained from H_2MoO_4 and purified by sublimation.[33]
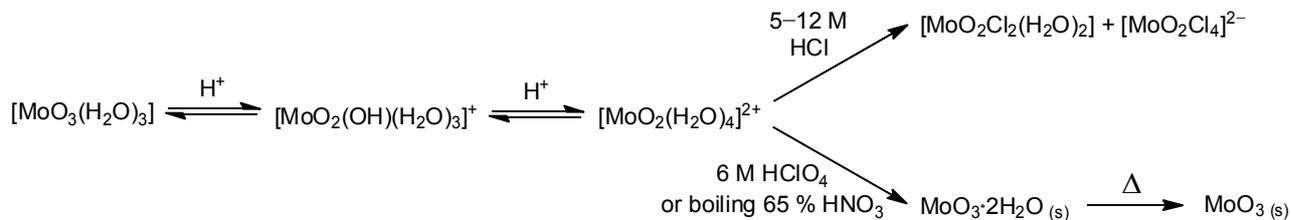
Fig. 5. Reactions of $[MoO_4]^{2-}$ in acidic solutions

When solutions of $[MoO_4]^{2-}$ are acidified in the presence of tetrahedral oxyanions or metal cations, various polyanions containing the heteroatom in a central tetrahedral hole forms, which are called heteropolymolybdates.[23] More than 65 elements from all the groups of the periodic table (except the noble gases) are implicated as heteroatoms in such structures. The preparation (2) and structure (see figure 6) of ammonium phosphomolybdate are reported as an example.

$$12\ (NH_4)_2MoO_4 + H_3PO_4 + 21\ HNO_3 \longrightarrow (NH_4)_3PMo_{12}O_{40} + 21\ NH_4NO_3 + 12\ H_2O \quad (2)$$
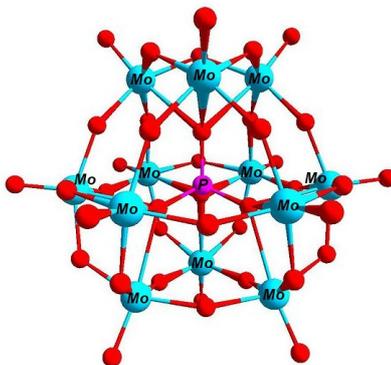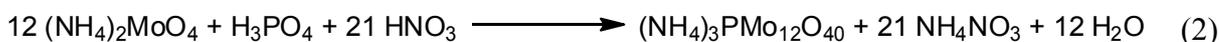
Fig. 6. The α-Keggin structure of the phosphomolybdate ion, $[PMo_{12}O_{40}]^{3-}$. Oxygen atoms are not labeled [1]

Equilibria involving $[MoO_4]^{2-}$ and isopolymolybdates in aqueous solutions are rapidly established and are complete in a matter of minutes. Tungsten(VI) shares with molybdenum(VI) a similar aqueous chemistry but its reactions are much slower than those involving molybdenum. Chromium(VI) shows a different and simpler aqueous chemistry: $[CrO_4]^{2-}$ undergoes slow acid hydrolysis and condensations leading to $[Cr_2O_7]^{2-}$, $[Cr_3O_{10}]^{2-}$ and $[Cr_4O_{13}]^{2-}$ in which chromium remains tetrahedral with corner (oxo) sharing.[4]

In accordance with periodic trends, the chromate and dichromate ions are fairly strong oxidizing agents[1] (3) while molybdate (4) and tungstate (5) are much more stable towards reduction.[183]

$$[Cr_2O_7]^{2-} + 14\ H_3O^+ + 6\ e^- \longrightarrow 2\ Cr^{3+} + 21\ H_2O \qquad E° = +\ 1.33\ V \qquad (3)$$

$$[MoO_4]^{2-} + 2\ H_2O + 2\ e^- \longrightarrow MoO_{2(s)} + 4\ OH^- \qquad E° = -\ 0.818\ V \qquad (4)$$

$$[WO_4]^{2-} + 4\,H_2O + 6\,e^- \longrightarrow W_{(s)} + 8\,OH^- \qquad E° = -\,1.060\;V \qquad (5)$$
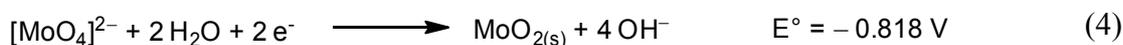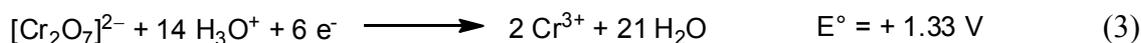
Reduction of aqueous molybdate(VI) solutions by a variety of reagents leads to the production of an intense blue, sometimes transient, and probably colloidal products, called molybdenum blues.[1] They appear to be oxide / hydroxide species with mixed valence [Mo(VI) / Mo(V)] and a precise explanation of their colour is lacking.[34,a]

Section 1.2 - Molybdenum-oxygen multiple bonds

An essential feature of molybdenum(VI) chemistry is ligand-to-metal multiple bonding. Terminal oxo groups are ubiquitous ligands in aqueous environments[2] but multiply bonded S and N groups are also known.[36] Because of the strength of this multiple bond, oxo terminal ligands occur in a wide range of compounds and persist through a variety of chemical reactions.[3] Vibrational, electronic, magnetic and chemical properties of molybdenum(VI) and molybdenum(V) compounds have been interpreted in terms of the Mo−O bonding interaction.[3]

An oxo ligand, O^{2-}, can be a six-electron donor through one σ and two π bonds to the metal.[37] For a d^0 metal, all d_π orbitals, being empty, are π-acceptors and consequently the metal-oxygen bond will have a multiple bond character.[38]

Molybdenum(VI) complexes with one ($[MoO]^{4+}$), two ($[MoO_2]^{2+}$) three ($[MoO_3]$) or four ($[MoO_4]^{2-}$) terminal oxo ligands are known.[3] The extent of π-bonding between molybdenum and oxygen decreases with increasing the number of terminal oxygens, due to the sharing of metal d_π orbitals.[39]

For dioxo octahedral complexes, the *cis*-configuration is preferred to the *trans* if there are no metal d-electrons: the strongly π-donating oxo ligands have the exclusive use of one d_π orbital each and share a third orbital; in the *trans*-form they would have to share two d_π orbitals and leave one of them as 'non-bonding'.[40] Thus the MO_2 group is invariably *cis* for molybdenum(VI) in order to maximize π-donation. For trioxo octahedral species, the *fac*-configuration allows an equal sharing of the metal d_π orbitals and on these grounds is to be preferred to the *mer*-form for d^0 complexes.

Multiple bonding to a given ligand is at the expense of bonds to other ligands. Four multiply bonded groups result in the exclusion of other ligands and in the formation of tetrahedral species such as $[MoO_4]^{2-}$. When less Mo=O fragments are present, other ligands may coordinate and the individual bonds to the oxygen atoms become stronger. Thus the average Mo−O bond distance

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a   It is known that the colour of pure Mo(VI) species is faint yellow or brown whereas the colour of pure Mo(V) species is red.[35]

decreases in the order $[MoO_4]^{2-} > MoO_3L_3 > MoO_2L_4 > MoOL_5$.[41]

Strong trans influences[b] are observed at sites *trans* to terminal oxo ligands.[36] Crystallographic measurements of bond lengths have established a trans influence series CO, $N_2 < NO < RN^{2-} < O^{2-} < N^{3-}$ which shows increasing effect with the formation of retrodative (L←M) < donor (L→M) bonds.[44] Thus, in a $MoOL_5$ or MoO_2L_6 complex, the ligands L, if not identical, will arrange themselves with the weaker π-donor ligands *trans* to the multiply bonded groups and the stronger π-donor ligands *cis* to the multiply bonded groups and *trans* to one another. Competition for metal d_π orbitals is minimized by this arrangement.

Fragments $[MoO_2]^{2+}$ and $[MoO_3]$ may be considered functional groups[45] as they can be transformed into other groups by oxygen atom substitution (e.g. with S^{2-} or O_2^{2-}),[46] derivatization or elimination. This situation is mirrored in the aqueous chemistry of molybdenum(VI). For example, multiply bonded oxo ligands are subject to protonation and elimination, as H_2O molecules, like the $[MoO_4]^{2-}$ anion is protonated in aqueous solution to give $[MoO_3(OH)_3]$, $[MoO_2(OH)(OH_2)_3]^+$ and finally $[MoO_2(OH_2)_4]^{2+}$ (see figure 7).
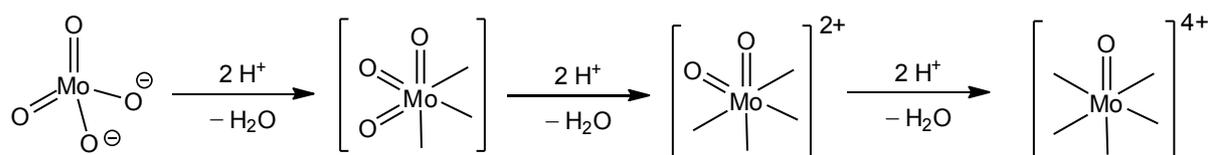
Fig. 7. Successive protonation and elimination reactions of $[MoO_4]^{2-}$

The formation of a *fac*-MoO_3 core from $[MoO_4]^{2-}$ requires two hydrogen ions (6) whereas a *cis*-MoO_2 species requires four (7). Oxo ligands are removed as water molecules.

$$[MoO_4]^{2-} + 2\,H^+ \longrightarrow [MoO_3] + H_2O \tag{6}$$

$$[MoO_4]^{2-} + 4\,H^+ \longrightarrow [MoO_2]^{2+} + 2\,H_2O \tag{7}$$
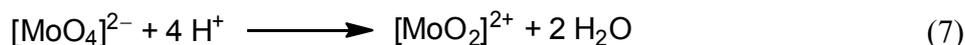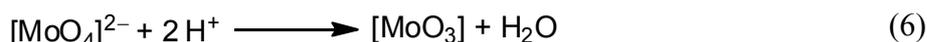
In acidic solutions, condensation reactions of $[MoO_4]^{2-}$ lead to polyoxomolybdates, which have both terminal and bridging oxygens. The formation of the heptamolybdate anion is reported in (8).

$$7\,[MoO_4]^{2-} + 8\,H^+ \longrightarrow [Mo_7O_{24}]^{6-} + 4\,H_2O \tag{8}$$
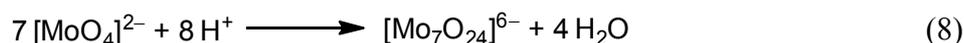
Similarly, the oxo ligands in complexes undergo protonation and condensation to produce μ-oxo species (and a water molecule).[3,47] An example is reported in figure 8.

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b The *trans influence* is the weakening and lengthening of a bond *trans* to a given ligand.[42] A ligand with better orbital overlap with the metal ion destabilizes the bond opposite to itself while enhancing the stability of its own bond.[43]
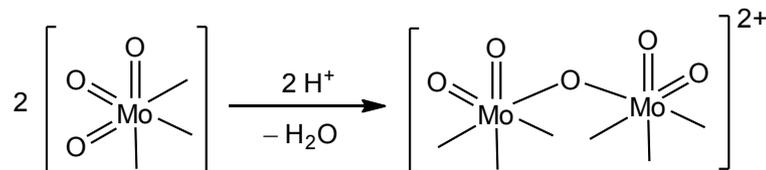
Fig. 8. The condensation of two [MoO$_3$] groups yields the oxo bridged species [Mo$_2$O$_5$]$^{2+}$

Section 1.3 - Some features of molybdenum(VI) complexes

The majority of molybdenum(VI) complexes are six-coordinate species with a distorted octahedral geometry.[36,48,49] Nonoctahedral molybdenum(VI) compounds occur when:

- Four strongly π-donating groups are present. Examples are compounds like [MoO$_x$S$_{4-x}$]$^{2-}$ (X = 0-4) and [MoO$_2$(NPPh$_3$)$_2$].[50]

- Chelate size and steric constraints disfavour the occupation of octahedral sites. This happens with chelates of very small ring size, such as peroxo (O$_2^{2-}$) and dithiocarbamato (R$_2$NCS$_2^-$) ligands, which lead to pentagonal bipyramidal forms (see figure 9).[41,51]

- Interligand steric hindrances or dentate-dentate bonding disfavour normal ligand arrangements.
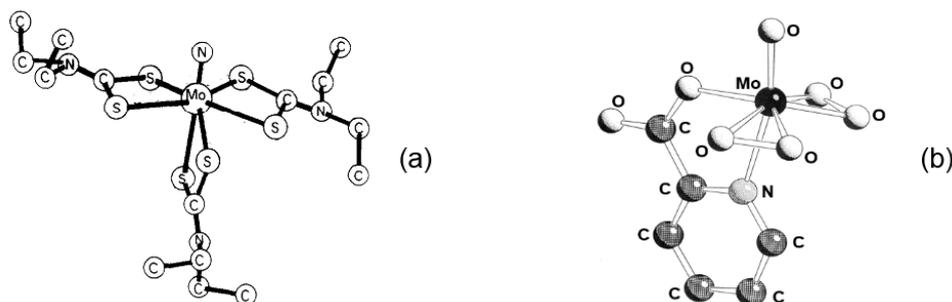
Fig. 9. Examples of pentagonal bipyramidal molybdenum(VI) complexes: (a) structure of [MoN(S$_2$CNEt$_2$-κS,κS')];[52] (b) structure of the [MoO(O$_2$)$_2$(Pic)]$^-$ anion[53]

Molybdenum(VI) complexes having one terminal oxygen are few. Examples include the monooxohalides MoOX$_4$ (X = F, Cl; see figure 10) and the peroxo complexes.[53]
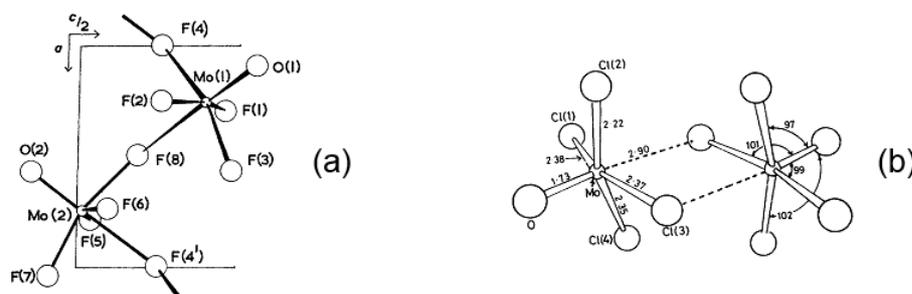
Fig. 10. (a) The polymeric structure of fluorine-bridged MoOF$_4$;[54] (b) the pseudodimeric structure of MoOCl$_4$ [55]

Several *cis*-dioxo Mo(VI) complexes are known. These are typically prepared by ligand addition, exchange and / or metathesis at *cis*-MoO$_2$ starting materials such as MoO$_2$Cl$_2$ or [MoO$_2$(acac)$_2$]. A distorted octahedral geometry results, due to the short Mo−O bonds and the O−Mo−O bond angles varying between 95 ° and 114 °.[41]

Many MoO$_2$ complexes with monodentate ligands have formula MoO$_2$X$_2$L$_2$ where X = halogen and L = neutral ligand. Examples are [MoO$_2$Cl$_2$(diglyme)],[56] [MoO$_2$F$_2$(THF)$_2$],[57] [MoO$_2$Br$_2$(DMF)$_2$][58] and [MoO$_2$Cl$_2$(OP(OPh)$_3$)$_2$],[59] some of which are reported in figure 11.
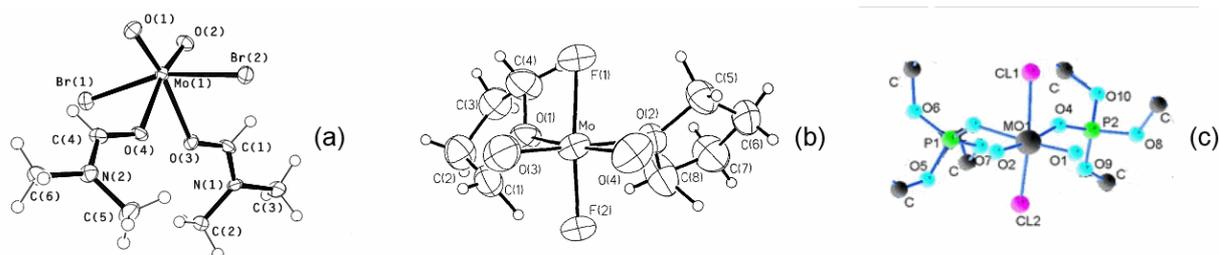
Fig. 11. (a) One of the four molecules in the asymmetric unit of [MoO$_2$Br$_2$(DMF)$_2$];[58] (b) the structure of [MoO$_2$F$_2$(THF)$_2$];[57] (c) the structure of [MoO$_2$Cl$_2$(OP(OPh)$_3$)$_2$] - phenyl rings have been omitted for clarity [59]

Due to the aforementioned trans influence, the weakest π-donor ligands (L) coordinate preferentially to the sites *trans* to the π-donor oxo ligands, stronger π-donor ligands (X) being mutually *trans* and *cis* to the oxo groups. Thus, almost all 6-coordinate complexes can be described in terms of the *cis,trans,cis*-MoO$_2$X$_2$L$_2$ structure[60] (see figure 12(a)) except when steric demands force the adoption of the electronically unfavourable *cis,cis,cis* structure[61] (see figure 12(b)).
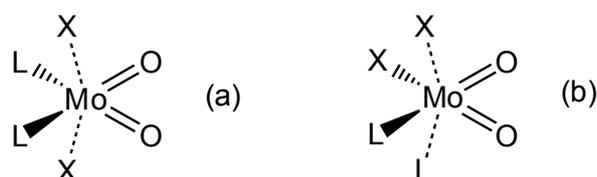
Fig. 12. (a) *Cis,trans,cis* and (b) *cis,cis,cis* structures for a MoO$_2$X$_2$L$_2$ complex

fac-Trioxo Mo(VI) complexes are colourless and the pyramidal [MoO$_3$] fragment is invariably "flattened", resulting in a relative shift of the molybdenum atom toward the plane of oxo ligands.[48] Trioxo complexes have been generally prepared in the presence of chelating ligands.[48]

Molybdenum(VI) complexes with chelating ligands

The inevitable presence of two or three terminal oxo ligands in an octahedral geometry leaves only a few coordination sites available. These are readily occupied by polydentate ligands and mononuclear coordination complexes of formula [MoO$_2$(κ^2-L)$_2$] or [MoO$_3$(κ^3-L)] result. Many of these have been isolated and structurally characterized.

Bidentate ligands that form mononuclear complexes with the *cis*-dioxo structure include

N,N-diethyldithiocarbamate,[62] cysteine methyl ester,[63] 8-hydroxyquinolinate[64] and acetylacetonate.[65]
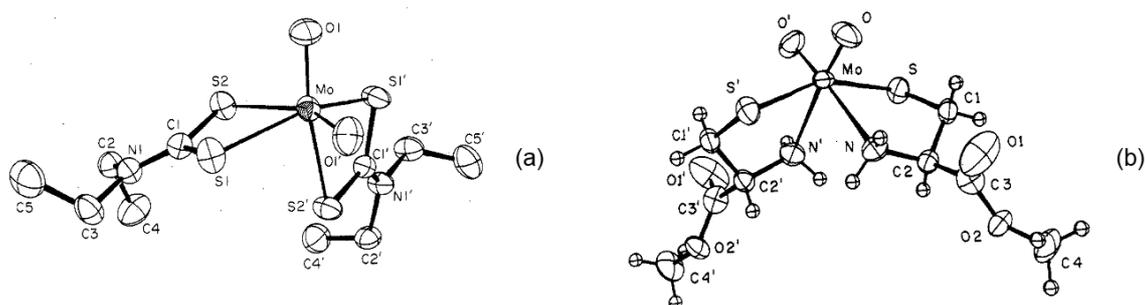
Fig. 13. (a) Structure of [MoO$_2$(S$_2$CNEt$_2$)$_2$];[62] (b) structure of [MoO$_2$(CysMe)$_2$][63]

A *fac*-trioxo structure is found in mononuclear complexes with terdentate ligands such as diethylenetriamine,[66] citrate,[67] triazacyclononane (and alkyl derivatives)[68,69] and in dinuclear complexes with hexadentate ligand, such as EDTA[70] and mannitol,[71] which bridge two [MoO$_3$] groups using three donor atoms for each (see figure 14).
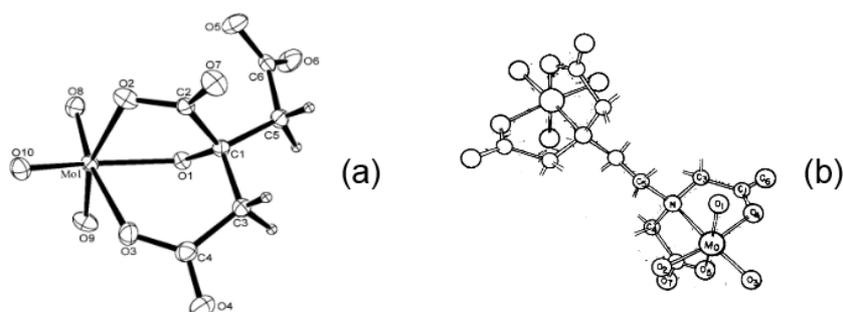
Fig. 14. Structures of the anions in (a) K$_4$[MoO$_3$(Cit)]·2H$_2$O [67] and (b) Na$_4$[Mo$_2$O$_6$(EDTA)]·8H$_2$O [70]

Many structural groups that are found in molybdenum(VI) complexes are derived from the sharing of one or more oxo ligands between two metal centres. A very common one[3] is [(MoO$_2$)$_2$(μ-O)]$^{2+}$ or simply [Mo$_2$O$_5$]$^{2+}$, which is found in the oxalate Rb$_2$[Mo$_2$O$_5$(C$_2$O$_4$)$_2$(H$_2$O)$_2$],[72] nitrilotriacetate (PyH)$_2$[Mo$_2$O$_5$(HNTA)$_2$][73] and citrate K$_4$[Mo$_2$O$_5$(CitH)$_2$]·4H$_2$O[67] structures.
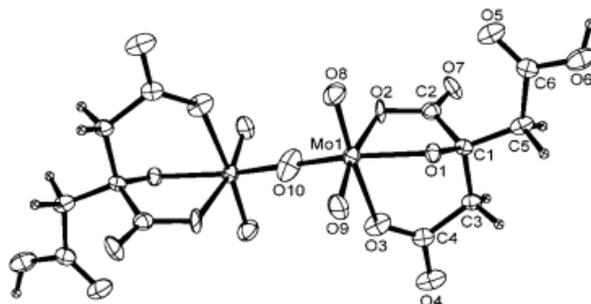
Fig. 15. The structure of the anion in K$_4$[Mo$_2$O$_5$(CitH)$_2$]·4H$_2$O.[67] The transformation from the monomeric (see figure 14(a)) to the dimeric citrate complex (this figure) and vice-versa can be accomplished by controlling the pH.

Dinuclear MoO$_2$ complexes with two oxo, hydroxo or alkoxo bridging ligands ([(MoO$_2$)$_2$(μ-OX)$_2$] group) are also known. Examples include [^{n}Bu$_4$N][Mo$_2$O$_4$(μ-O)$_2$(Pic-κN,κO)],[74]

[Mo$_2$O$_4$(μ-OMe)$_2$((MeCHO)$_2$-κO,κO')$_2$][75] and some iso[76] and heteropolyanions[77] for bridging OH ligands.
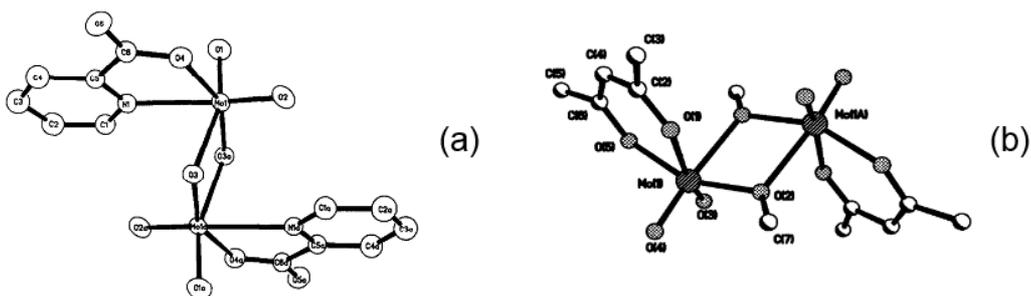
Fig. 16. (a) Structure of the anion in [^{n}Bu$_4$N][Mo$_2$O$_4$(μ-O)$_2$(Pic-κN,κO)];[74] (b) structure of [Mo$_2$O$_4$(μ-OMe)$_2$((MeCHO)$_2$-κO,κO')$_2$] [75]

Section 1.4 - Molybdenum(VI) and α-amino acids: a well-known class of compounds

α-Amino acids (generic formula H$_2$NCHRCOOH in most cases,[c] where the organic substituent R is known as "side-chain") are molecules of major importance in biochemistry.[78] They include the 20 "standard" proteinogenic amino acids, which are the building blocks of proteins and peptides.[d]

α-Amino acids are also potential chelating ligands and their complexation by numerous metal ions has been extensively studied.[79-82] Some areas of the chemistry of molybdenum(VI) with α-amino acids have been well investigated and several complexes containing amino acids as ligands have been identified in solution and / or in the solid state. Complexes of molybdenum(VI) and α-amino acids that have been structurally determined, to the best of my knowledge, can be divided into the following groups:

- Compounds with O$_2$$^{2-}$ as co-ligand (oxoperoxo complexes)

- Compounds with high nuclearity, consisting of:

  ○ Isopolymolybdates

  ○ Heteropolymolybdates

Complexes belonging to each group (and analogues not structurally determined) have many features in common, including the coordination of the amino acid, the moybdenum-oxygen framework and preparative methods. A brief summary for each group is given below.

---

c   Proline has a secondary amine group (NHR') because of the cyclization of the side-chain

d   In this work, the attention is focused on this group of molecules. The term α-amino acid (or simply amino acid) is used in this chapter to refer specifically to these species. Both enantiomers of chiral amino acids are included in the discussion

Oxoperoxo-amino acid complexes

Oxoperoxo complexes have a mononuclear structure in which one zwitterionic amino acid is monocoordinated through the carboxylate group. The molybdenum atom is involved in a distorted pentagonal bipyramidal geometry. The carboxylic oxygen and two bidentate side-on peroxo ligands occupy the equatorial positions while an oxo group and a water molecule are in *trans-* to each other in the apical positions. The structure of these neutral compounds of formula $[MoO(O_2)_2(aaH)(H_2O)]$ is known for glycine,[83,84] alanine,[84] and proline,[83,84] which is shown in figure 17.

Fig. 17. The crystal structure of $[MoO(O_2)_2(ProH)(H_2O)]$[84]

A similar structure has been proposed for complexes prepared with other amino acids: valine,[84] leucine,[84] aspartic acid,[85] asparagine,[84] glutamine,[84] glutamic acid[84,86] and serine.[84]

All the $[MoO(O_2)_2(aaH)(H_2O)]$ complexes are well soluble in water[83] and have been prepared by the reaction of MoO_3 with the amino acid, in stoichiometric ratio, in 30 % hydrogen peroxide solution (9).

$$MoO_3 + aaH + 2\,H_2O_2 \xrightarrow[\text{30 \% H}_2\text{O}_2]{\text{RT}} [MoO(O_2)_2(aaH)(H_2O)] + H_2O \qquad (9)$$

Tarafder et al[87] obtained neutral monoperoxo complexes with a chelating amino acidate ligand from a basic ethanol / water reaction mixture (see figure 18). Glycine and leucine, two amino acids with a non polar side-chain, formed $[MoO(O_2)(aa\text{-}\kappa N,\kappa O)_2]$ while tyrosine (TyrH$_2$) formed $[MoO(O_2)(Tyr\text{-}\kappa N,\kappa N',\kappa O)(H_2O)]$, in which the ionized side-chain group is also involved in coordination.

$$[MoO(O_2)(Tyr)(H_2O)] \xleftarrow[\text{RT}]{\substack{\text{TyrH}_2 \\ \text{in EtOH + KOH}}} \underset{\substack{\text{in 30 \% H}_2\text{O}_2}}{MoO_3} \xrightarrow[\text{RT}]{\substack{2\,\text{aaH (GlyH, LeuH)} \\ \text{in EtOH + KOH}}} [MoO(O_2)(aa)_2]$$

Fig. 18. Scheme of reactions between MoO_3 and amino acids in basic peroxide solutions

Serdiuk et al.[88] prepared poorly water-soluble polynuclear complexes having a

metal/amino acid ratio of 2 with serine and methionine and equal to 3 with lysine and histidine, in a pH = 2 peroxide solution (see figure 19). However, these products have been characterized only with elemental analysis and IR spectroscopy.

$$MoO_3 \text{ in } 30\% \ H_2O_2 \quad \begin{array}{l} \xrightarrow{aaH} [Mo_2O_2(\mu\text{-}O)_2(O_2)_2(aaH)(H_2O)_2] \qquad aaH = SerH, MetH \\ \xrightarrow{RT, \ pH = 2} \\ \xrightarrow{aaH_2} [Mo_3O_3(\mu\text{-}O)_4(O_2)_2(aaH_2)(H_2O)_4] \quad aaH_2 = LysH_2, HisH_2 \end{array}$$

Fig. 19. Scheme of reactions of MoO_3 with amino acids in acidic peroxide solutions

The preparation of heteronuclear Zn(II)-Mo(VI) or Cu(II)-Mo(VI) peroxocomplexes containing glycine or its dipeptide (Glycylglycine) as ligands has also been reported.[85,89,90]

Isopolymolybdate-amino acid complexes

Many isopolymolybdates functionalised with amino acids have been structurally characterized.[91-100] Their structure is built up of a Mo_8O_{26} fragment to which one, two or four zwitterionic amino acid molecules are bonded via a monodentate coordination of the carboxylate group. Compounds having this structure are known for L-methionine,[91] L-lysine,[92] glycine,[93,97] DL-proline,[99] DL-[98] and L-alanine,[100] which structure is shown in figure 20.

Fig. 20. The crystal structure of the anion in $K_4[Mo_8O_{26}(AlaH)_2]\cdot4H_2O$ [100]

Most of these complexes have been prepared using MoO_3, K_2MoO_4 or $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ as molybdenum(VI) sources, under hydrothermal conditions[93,97,100] and / or in mildly acidic aqueous solutions (pH = 3-6).[91,93,98-100] The preparation of $K_4[Mo_8O_{26}(AlaH)_2]\cdot4H_2O$ is reported in (10).

$$8 \ Na_2MoO_4 + 2 \ AlaH + 4 \ KCl + 12 \ HNO_3 \xrightarrow[\text{pH = 2}]{116 \ °C, \ 1 \ h} K_4[Mo_8O_{26}(AlaH)_2]\cdot4H_2O + 2 \ H_2O + 12 \ NaNO_3 + 4 \ NaCl \quad (10)$$

Mixed valence [Mo(VI) / Mo(V)] polyanions with a higher nuclearity and zwitterionic glycine ligands have been prepared in aqueous solution with hydrazine ($N_2H_2\cdot2HCl$ or $N_2H_2\cdot H_2SO_4$) as reducing agent and structurally characterized.[94-96]

Heteropolymolybdate-amino acid complexes

The third group of structurally-determined molybdenum(VI)-amino acid complexes consists of heteropolymetalate compounds.[101-103] All these coloured and water soluble complexes are isostructural and have been prepared in similar conditions.

Cindríc et. al[101] synthesized a glycine-containing heteropolymolybdate of formula $K_2[HMo_6VO_{22}(GlyH)_3]\cdot 8H_2O$ (see figure 21). In this compound, each *cis*-MoO_2 group is linked to a second one by two oxo bridging ligands and to a third one by one oxo bridging ligand. This give rise to a chain of three $[(Mo_2O_4(\mu\text{-}O)_2)(\mu\text{-}O)]^{2-}$ dimers enclosed in a ring. The pair of molybdenum atoms bridged by two oxo ligands are also bridged by a zwitterionic glycine molecule coordinated through both oxygens of its carboxylate group. An oxovanadium(V) cation (VO^{3+}) is located at the centre of this ring and vanadium is coordinated to one oxo bridge for each Mo_2 dimer, giving it a tetrahedral arrangement.

Fig. 21. The crystal structure of the $[Mo_6VO_{22}(NH_3CH_2COO)_3)]^{3-}$ anion[101]

Kortz et al[102,103] synthesized analogous heteropolymolybdates of general formula $[XMo_6O_{21}(O_2CCHRNH_3)_3]^{n-}$ with glycine, β-alanine, 4-aminobutyric acid, L-alanine, L-Lysine and various heteroatoms (X = Se, Te, As, Sb, Bi and RP with R = OH, H, Me, Et). These compounds have been prepared at high temperatures from aqueous suspensions of MoO_3 or acidic solutions of Na_2MoO_4, containing KCl, the heteroatom as oxyanion (e.g. V_2O_5 for VO^{3+}, NaH_2PO_4 for $P(OH)^{4+}$) and the amino acid (see figure 22).

$$MoO_3 + V_2O_5 + GlyH \xrightarrow[\text{KCl}]{90\ °C,\ 6\ h} K_2[HMo_6VO_{22}(GlyH)_3]\cdot 8H_2O$$

$$Na_2MoO_4 + H_2SeO_3 + GlyH \xrightarrow[\text{KCl, pH = 3}]{100\ °C,\ 1\ h} K_2[SeMo_6O_{21}(GlyH)_3]\cdot 8H_2O$$

Fig. 22. Two similar routes followed for the preparation of $[XMo_6O_{21}(O_2CCH_2NH_3)_3]^{n-}$

The formation of compounds with such a structure is not a prerogative of zwitterionic

ligands, since an anion containing three acetate ligands and a structure analogue to $[Mo_6VO_{22}(NH_3CH_2COO)_3)]^{3-}$ has been recently isolated as tris-diammonium ethane salt.[104]

Section 1.5 - Molybdenum(VI) and α-amino acids: looking for simple MoO₂ and MoO₃ complexes

Excluding complexes with hydrogen peroxide and high nuclearity compounds, to the best of my knowledge, no other crystal structure containing molybdenum(VI) and α-amino acids is currently known. This is somewhat surprising, considering the high number of mononuclear or dinuclear complexes with $[MoO_2]^{2+}$ and $[MoO_3]$ groups that have been isolated in the presence of chelating ligands (as discussed in section 1.3).

Studies in aqueous solution

Equilibria between $[MoO_4]^{2-}$ and α-amino acids in aqueous solutions with different pH values have been extensively studied with several techniques such as spectrophotometry,[105-124] polarimetry,[105,106,108,113-117,119,121,124,125] circular dichroism,[109,126] ^1H, ^{13}C and ^{95}Mo NMR,[106,109,126-128] potentiometric[111,112,117,119,121,124,125,129-131] and calorimetric[112] titrations.

These works have focused attention on amino acids with a polar side-chain, i.e. those that can potentially act as triscoordinating ligands: cysteine, histidine, aspartic acid, asparagine and glutamic acid. The following general trend has been observed:

- In mildly acidic solutions (4.5 < pH < 7), anionic complexes of formula $[MoO_3(L)]^{x-}$ have been identified and their formation constants have been calculated.[109,114,115,117,118,120,124,125,127,128,131] The amino acid is coordinated by the amino, carboxylate and side-chain groups, as shown in figure 23. The 1 : 1 monomeric complex reaches its maximum molar fraction at pH around 5-6 and it is often accompanied by the presence of polynuclear complexes and numerous other species with a different degree of protonation.[105,110-113,116,119,121,126]

Fig. 23. Proposed structures for $[MoO_3(aa)]^{2-}$ anions (aaH₂ = aspartic acid (a), cysteine (c)) and $[MoO_3(HisH)]^-$ (b)

17

- Almost no complex formation is observed in basic solutions (pH > 7), due to the exceedingly high stability of $[MoO_4]^{2-}$.[106,111,113-117,119,121,124,131] $[MoO_3(Cys)]^{2-}$ is an exception, being stable up to pH = 8.5.[126,127]

- In acidic solution (depending on the concentration), cysteine oxidises to cystine, causing reduction of molybdenum(VI) to molybdenum(V) with formation of molybdenum blue.[105,108,109,127] For histidine, aspartic and glutamic acid, older works[106,124,131] claim that for pH < 4 no complex is formed due to the competitive formation of isopolymolybdates. More recent works[111,112,114,115] suggest the presence of some polynuclear complexes in acidic solution.

Amino acids with a non polar side-chain have been much less studied. No evidence for complex formation between pH = 4 and 7 has been reported for valine, leucine and phenylalanine[108] and at pH = 6 for glycine and alanine.[128]

Complexes isolated in the solid state

The colourless and water-soluble complexes $K_2[MoO_3(Asp)]·H_2O$ and $Na[MoO_3(HisH)]·H_2O$ have been crystallized by slow evaporation of an aqueous solution at pH = 6 in stoichiometric conditions (see figure 24).[132] These compounds contain the $[MoO_3(L)]^{x-}$ anion already identified in solution.

$$Na_2MoO_4 + HisH_2 \xrightarrow[pH = 6]{\Delta} Na[MoO_3(HisH)]·H_2O$$

$$K_2MoO_4 + AspH_2 \xrightarrow[pH = 6]{\Delta} K_2[MoO_3(Asp)]·H_2O$$

Fig. 24. Preparation of $K_2[MoO_3(Asp)]·H_2O$ and $Na[MoO_3(HisH)]·H_2O$ [132]

Neutral bis(glycinato)dioxomolybdenum(VI), $[MoO_2(Gly-\kappa N,\kappa O)_2]$ has been obtained with a solid-state substitution reaction involving $[MoO_2(MeCH(O)CH(O)Me-\kappa O,\kappa O')_2]$ (see figure 25).[132] This complex is highly susceptible to hydrolysis and no glycinate derivative has been obtained from aqueous solutions.

Fig. 25. Solid-state exchange reaction between glycine and the MoO_2 complex of 2,3-butanediol

Kay and Mitchell[133] described the preparation of $Na_2[MoO_2(Cys)_2]\cdot DMF$. This product has been obtained from an aqueous pH = 7 solution of sodium molybdate and cysteine and reprecipitated from a DMF solution. A bidentate $\kappa N, \kappa S$ coordination with an uncoordinated carboxylate group is proposed for cysteine (see figure 26), relying on IR characterization.

$$Na_2MoO_4 + 2\ ^{+}H_3NCH(CH_2SH)COO^{-} \xrightarrow[\text{2) DMF / Me}_2\text{C(OMe)}_2]{\text{1) pH = 7}}$$

Fig. 26. Preparation and proposed structure of $Na_2[MoO_2(Cys)_2]\cdot DMF$[135]

Some complexes have been isolated from acidic aqueous solutions of $[MoO_4]^{2-}$ and amino acids.[133-136] These colourless or yellowish diamagnetic compounds have a molybdenum/amino acid ratio of 2 and are insoluble in water or common organic solvents but soluble in alkali where they decompose. Their IR spectra have some common features.[e] However, the structures proposed for these complexes are based only on infrared spectral interpretation and results are quite controversial.

Furuhashi et al[134] obtained a series of compounds by refluxing an aqueous pH = 1 solution containing Na_2MoO_4 and glycine, DL-alanine, DL-methionine or L-leucine in various molar ratio (from 4 : 1 to 1 : 4). Following the same procedure, Udupa et al.[135] obtained similar complexes with glutamic acid and β-alanine. These authors suggest the presence of one terminal oxo ligand, a Mo−O−Mo bridge and the coordination of the amino acidate anion through one carboxylic oxygen and the amino group. However, they eventually propose a polymeric structure (reported in figure 27) in which both oxygens of the carboxylate group (and also the amino group) are involved in coordination.

Fig. 27. Proposed structure for $Mo_2O_4(OH)_3(aa)$ complexes (aaH = GlyH, AlaH, MetH, LeuH) and for $Mo_2O_4(OH)_3(GluH)$ [134,135]

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e   The Mo−O stretching region shows four strong bands, around 950, 917, 890 and 760 cm^{-1}.[133,134,136] The carboxylate stretching absorptions have a little shift from those of the free ligand while the N−H stretching bands are weak and broad[133-136]

A colourless complex of formula $Mo_4O_8(OH)_6(Ala)_2$ was prepared from the reaction of $[MoO_4]^{2-}$ with alanine in boiling 1 M HCl or from MoO_3 and alanine in boiling water.[133] The molybdenum-oxygen stretching vibrations have been attributed to a *cis*-MoO_2 group, another terminal Mo=O group and a Mo−O−Mo bridge. The authors suggest that the amino group and both oxygens of the carboxylate group are involved in coordination but they eventually propose a structure with κN,κO-alaninate molecules (see figure 28).

Fig. 28. Proposed structure for the $Mo_4O_8(OH)_6(Ala)_2$ complex[133]

Castillo et al.[136] obtained similar products by heating at 70-80 °C aqueous pH = 2 solutions of Na_2MoO_4 and amino acids (glycine, alanine, proline, valine, leucine) in a 2 : 1 molar ratio. They suggest a dinuclear structure in which two *cis*-MoO_2 group are held together by one bridging oxo ligand and the bidentate carboxylate group of the zwitterionic amino acid (see figure 29). However, it is not clear why they proposed the presence of pentacoordinated molybdenum atoms.

Fig. 29. Proposed structure for $Mo_2O_4(\mu\text{-}O)(aaH)(OH)_2$ complexes (aaH = GlyH, AlaH, ProH, LeuH, ValH)[136]

Recently, a product containing histidine and molybdenum in a 2 : 1 molar ratio has been obtained at room temperature from a pH = 2 aqueous solution of sodium molybdate and histidine (11).[137] On the basis of molybdenum content and IR spectrum, the authors proposed the structure $[MoO_2(HisH)_2]$, with a bidentate κN,κO coordination of histidinate anions. However they also attributed the absorption at 770 cm^{-1} to the stretching vibration of a Mo−O−Mo group and thus it is probable that also this compound with M/L = 1 : 2 is polynuclear.

$$2\,H^+ + [MoO_4]^{2-} + 2\,HisH_2 \xrightarrow[\text{pH = 2.2}]{\text{RT}} [MoO_2(HisH)_2] + 2\,H_2O \qquad (11)$$
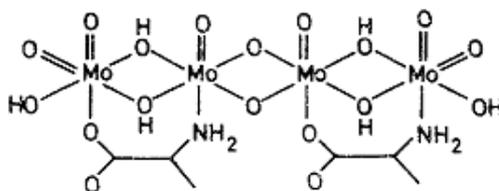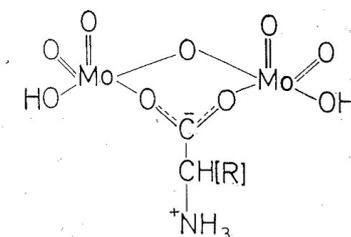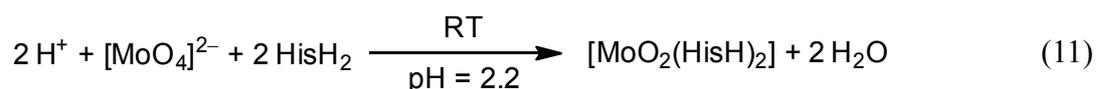
Section 1.6 - Molybdenum(VI) complexes as catalytic precursors for oxidations of alkenes

d^0 Transition metal complexes, especially molybdenum(VI) and vanadium(V), are widely used in catalytic[16,138] and stoichiometric[45] oxidations of organic substrates such as olefins, sulphides, alcohols, alkanes and amines.

The direct catalytic epoxidation of alkenes has been the main process to prepare epoxides or diols. Gas-solid reactions with dioxygen and silver-based catalysts take place only for small alkenes, such as ethylene and propylene,[139,140] because, under these conditions, higher alkenes are almost completely converted to carbon dioxide and water. Therefore, most of the catalytic conversion of higher alkenes to the corresponding epoxide has been performed in liquid phase. In liquid-phase oxidations, dioxygen is not effective as oxidant, being peracids and peroxides the most widely used.[141,142]

Some of the non-functionalised olefins that have been used as substrates in molybdenum(VI) catalysed oxidations include cyclohexene, cyclooctene, norbornene, 1-hexene, styrene and α-pinene.[143-146] Cyclohexene is by far the most used.

The nature of the catalytic-active species depends on the interaction of the metal precursor with the oxygen donor, so that, in many cases, high-valent oxometal or peroxometal species have been proposed as key intermediates (see figure 30).[147,148]
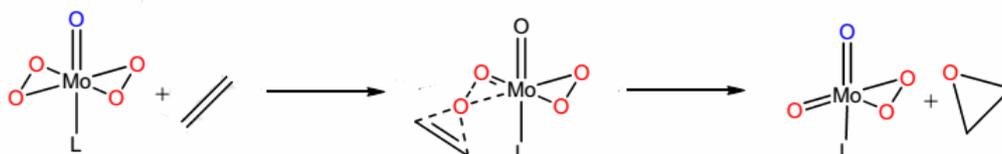
Fig. 30. The Sharpless mechanism for the epoxidation of olefins with [MoO(O$_2$)$_2$L] (L = H$_2$O, DMF, HMPT, Py)[149]

One of the preferred oxygen sources is *tert*-butyl hydroperoxide (TBHP), partly because it is environment-friendly, not very corrosive or hazardous and its reduction product, *tert*-butanol, can easily be separated and recycled for use in other industrial processes.[150]

Many dioxomolybdenum(VI) complexes have been used as homogeneous[137,151-164] or heterogeneous catalysts (e.g. supported on functionalised silica[165] or carbon nanotubes[159,166]) for the oxidation of cyclohexene with TBHP. These reactions have been carried out in hydrocarbons (toluene, decane) or chlorinated solvents (dichloromethane, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane) and some in solvent free-conditions.

A high selectivity (65-100 %) towards cyclohexene oxide is observed in many cases. The main by-products are *trans*-1,2-cyclohexanediol,[164] 2-cyclohexenol and 2-cyclohexenone.[137,161]

Some molybdenum(VI) compounds are effective catalysts even at room temperature[151,155] but the majority of reactions have been performed at 50-100 °C.

Another widely used oxidant is hydrogen peroxide.[164,167-174] For economic and environmental reasons, oxidation processes with H_2O_2 are classified as sustainable because hydrogen peroxide is, besides dioxygen, the oxidant with the highest *atom efficiency* (47 % of active oxygen), it is readily accessible and safe to use and leads to water as the only by-product.[175,176]

The selectivity towards cyclohexene oxide with hydrogen peroxide is generally lower than with TBHP and often the main reaction products are *trans*-[170] and / or *cis*-1,2-cyclohexanediol.[164] 2-Cyclohexenone and 2-cyclohexenol have been obtained in some cases as by-products due to the allylic oxidation of cyclohexene (see figure 31).[164,171,173]
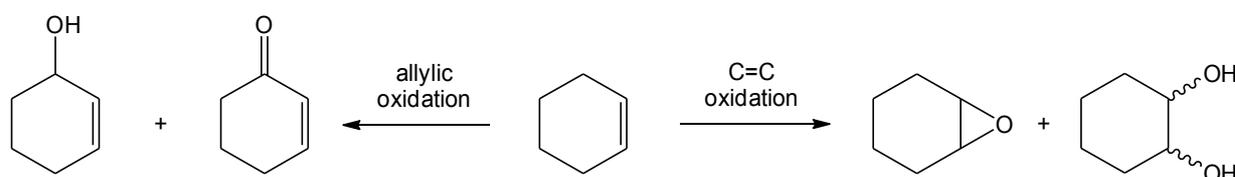
Fig. 31. Main oxidation products of cyclohexene in liquid-phase reactions with peroxides and molybdenum(VI)

A strong influence of the solvent on conversion and selectivity has been observed. Umbarkar et al[173] found a high conversion (91-95 %) using methanol or *tert*-butanol as solvents and a much lower one (67-72 %) using acetonitrile or chlorinated compounds (CCl_4, $CHCl_3$, CH_2Cl_2), the other conditions being equal ([CpMo(CO)$_3$(C≡CPh)] as catalyst precursor, 65 °C, 48 hours). However, the selectivity towards *cis*-1,2-cyclohexanediol is higher (60-68 % vs. 42-48 %) with the latter solvents, because the excess of alcohol causes the monoetherification of the diol, yielding 2-alkoxycyclohexanol. The formation of 2-alkoxycyclohexanol is more effective with lower alcohols (see figure 32).[167]

Cy(OH)$_2$, % selectivity :
^{t}BuOH (99); ^{i}PrOH (66); EtOH (34); MeOH (12)

Cy(OH)(OR), % selectivity :
^{t}BuOH (0); ^{i}PrOH (33); EtOH (65); MeOH (87)
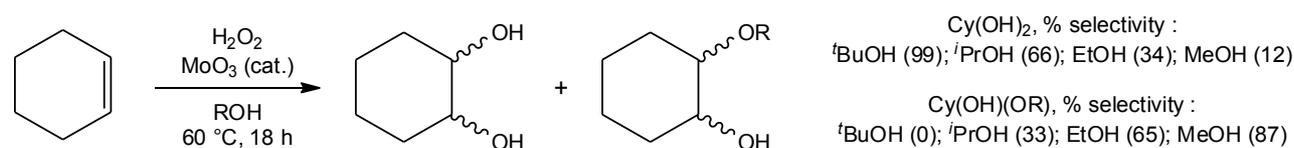
Fig. 32. The change in selectivity by using different alcohols as solvents, under equal conditions[167]

Section 1.7 - Aim of the Work

As described in section 1.5, many aspects of the chemistry of molybdenum(VI) with α-amino acids have not been investigated or a detailed knowledge is lacking. In particular, the products obtained from acid aqueous solutions of molybdate and amino acids have been poorly characterized. In addition, the correlation between the preparative conditions (pH, concentration, temperature ...) and the formation of these products has not been explained.

In view of the state of the art, it was decided to study in detail the formation of molybdenum(VI)-amino acids complexes in acidic aqueous solutions and to characterize the structure of these compounds. Moreover, the molybdenum(VI) complexes prepared were tested as catalytic precursors in oxidation reactions of cyclohexene.

CHAPTER 2

Experimental part

Section 2.1 - General considerations

All manipulations were performed in air with common laboratory glassware. All aqueous reactions were carried out using deionized water. The following reagents and solvents were used as purchased without further purification: 98 % $Na_2MoO_4 \cdot 2H_2O$, P_4O_{10}, CaH_2, *trans*-1,2-cyclohexanediol (*Alfa Aesar*), glycine, L-phenylalanine, L-leucine, L-proline (*Apollo Scientific*), $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, KSCN,[f] $SnCl_2 \cdot 2H_2O$,[f] NaOH, dimethyl sulphoxide (*Carlo Erba*), potassium hydrogen phthalate (*Fluka*), L-methionine, *N,N*-dimethyl-*L*-phenylalanine, $MoO_2(acac)_2$,[f] cyclohexene, 35 % H_2O_2, 65 % HNO_3, 37 % HCl, chlorobenzene, *n*-decane, methanol, 96 % ethanol, isopropanol, acetone, diethyl ether, D_2O, $CDCl_3$, DMSO-d$_6$ (*Sigma-Aldrich*). CuCl[f] was prepared according to the literature[177] and stored under an inert atmosphere. $(NH_4)_2MoO_4$ [178] and $MoO_3 \cdot H_2O$ [33] were prepared from $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ following literature procedures.

Analytical and physico-chemical measurements

Macherey-Nagel pH-test strips with various pH gradations between 1.0 and 5.5 were used for pH measurement except in section 2.9, where an *Orion* pH-meter equipped with *Hamilton* glass pH-electrode was used (pH range 0-14, temperature range 0-80 °C, Ag / AgCl / 3 M KCl internal reference). Before each measurement, the instrument was calibrated with standard pH buffer solutions (*Fluka*, pH = 4.0 and pH = 7.0).

IR solid state spectra were recorded on a *Perkin-Elmer* FT-IR spectrometer. The UATR sampling accessory was used in the 650-4000 cm^{-1} range. Spectra in the 360-650 cm^{-1} region were recorded in the transmission mode on Nujol mulls.

UV-Vis solution measurements were carried out on a *JASCO V-530* spectrophotometer using a pathlength of 1.0 mm and a bandwidth of 1.0 nm. Spectra were recorded with a scan speed of 250 nm/min in the 200-1100 nm range; otherwise the fixed-wavelength mode was used (e.g. for molybdenum analyses).

NMR solution spectra were recorded on a *Bruker Avance DRX400* instrument equipped with

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f   This reagent was used for molybdenum elemental analysis

a BBFO broad-band probe. The nondeuterated aliquot of the solvent was used to lock the field. The chemical shifts for ^1H and ^{13}C are given relative to tetramethylsilane (TMS).

NMR ^{13}C CP-MAS spectra were recorded by Dr C. Forte, ICCOM-CNR (Pisa) on a *Bruker AMX300WB* instrument with a 90 ° pulse of 3.4 μs length, an initial contact time of 2 ms and a 4 s delay between scans. A rotating speed of 9 kHz was used except when problems due to packaging of the rotor and / or consistency of the sample, forced the use of a 5 kHz speed. The number of scans (200-2000) depended essentially on the amount of sample, the type of signals and the cross-polarization efficiency. Carbonyl and aromatic signals often showed rotational bands at ±119 ppm and ±66 ppm for a 9 kHz and 5 kHz rotation respectively (rotational bands are marked with an asterisk in plotted spectra). NMR spectra of *N,N*-dimethyl-L-phenylalanine and related products were fully assigned via spectral editing techniques.[179,180]

Gas chromatographic analyses were performed on a *Perkin Elmer Clarus 500* instrument equipped with a programmable split / splitless injector (PSSI), a *Supelco-24028* capillary column (L x I.D. 30 m x 0.25, d_f 0.25 μm) and a FID detector. The following temperature program was used: initial temperature 73 °C (hold for 0.10 min) then 6.0 °C/min to 77 °C, then 15 °C/min to 115 °C, then 45 °C/min to 300 °C (hold for 2.0 min). Injector temperature 220 °C, detector temperature 280 °C, total run time 9.41 min.

Polarimetric measurements were performed on a *Perkin Elmer - 141* instrument equipped with a *Colora* thermostat. Optical rotations were measured at 20 °C with a sodium lamp (589 nm), using a 4 mL volume cell with a 1.0 dm pathlenght.

Carbon, hydrogen and nitrogen analyses were performed on a *Carlo Erba model 1106* instrument. Molybdenum was analysed according to the method proposed by Crouthamel e Johnson[181] after dissolution of a weighted amount of sample (30-60 mg) in 100 mL of 4 M HCl. A calibration curve was obtained using $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ as standard ($R^2 = 0.999$). As a reference compound, the acetylacetonate $MoO_2(acac)_2$ was used (Anal. Calcd for $C_{10}H_{14}MoO_4$: Mo 29.4 %; Found: 30.2 %).

DFT calculations were performed by Dr M. Bortoluzzi, Università Cà Foscari (Venezia). The geometric optimizations were carried out in gas phase using the hybrid EDF2 DFT functional in conjunction with the *basis set split-valence double-ζ* polarized LACVP** (6-31G** on light atoms, LANL2DZ on molybdenum), which provides the use of an *effective core potential* for the simulation of the inner electronic spheres of metal centres. In all cases, the molecules have been considered in the singlet state and the approach *restricted* has been adopted. The simulations IR equilibrium geometries were performed using the harmonic approximation. The software used for all calculations is *Spartan 08*.

Section 2.2 - General preparation of $Mo_2O_4(OH)_4(aaH)$ from Na_2MoO_4

A stock pH = 2.0 solution with [Mo] = 0.190 was prepared by dissolving $Na_2MoO_4 \cdot 2H_2O$ (6.00 g, 24.8 mmol) in 90.0 mL of water and by adding 40 mL of 1 M HNO_3. In a round-bottom flask, 2.00 mmol of amino acid were dissolved in 15 mL of water and pH = 2.0 was obtained by adding 2.0 mL of 1 M HNO_3. To this solution, 21.0 mL of the molybdate solution (4.00 mmol of Mo) were added and the resulting pale yellow solution ($[Mo]_0$ = 0.105) was stirred at room temperature. A pale yellow solid ($Mo_2O_4(OH)_4(aaH)$) was obtained after a certain time, depending on the amino acid used. After 20-24 hours, the reaction mixture was filtered. The pH of the solution was measured soon after mixing of the reagents (1-5 min) and after filtration. The solid was washed with acetone, diethyl ether and dried under vacuum with P_4O_{10}. Details for single preparations are given below.

Glycine - A solid was observed after 25 minutes. Initial pH = 1.8, filtrate pH = 3.2. Yield: 715 mg (90 %) of $Mo_2O_4(OH)_4(GlyH)$. Anal. Calcd for $C_2H_9Mo_2NO_{10}$: C, 6.02; H, 2.27; N, 3.51 %; Found: C, 6.03; H, 2.13; N, 3.67 %. ^{13}C NMR (CP-MAS solid state): δ/ppm = 172.0 (CO); 41.3 (CH_2). IR (ATR and Nujol): $\tilde{\upsilon}$/cm^{-1} = 3580 (w, br); 3428 (w, br); 3363 (w, br); 3231 (w, br); 3012 (w, br); 2931 (w, br); 2753 (w, br); 2649 (w, br); 1676 (w); 1626 (m); 1592 (m); 1520 (sh); 1512 (m); 1496 (sh); 1455 (m); 1414 (m); 1341 (m); 1149 (w); 1119 (w); 1052 (w); 950 (s); 923 (s); 905 (s); 761 (w); 735 (sh); 558 (sh); 530 (s, br); 474 (sh).

L-Phenylalanine - A solid was observed after 2.5 hours. Initial pH = 1.9, filtrate pH = 2.5. Yield: 805 mg (90 %) of $Mo_2O_4(OH)_4(PheH)$. Anal. Calcd for $C_9H_{15}Mo_2NO_{10}$: C, 22.10; H, 3.09; N, 2.86 %; Found: C, 22.05; H, 2.85; N, 2.75 %. IR (ATR): $\tilde{\upsilon}$/cm^{-1} = 3553 (w, br); 3055 (w, br); 1606 (m); 1524 (m); 1497 (m); 1451 (w); 1423 (m); 1361 (m); 1346 (m); 1246 (w); 1143 (w); 1084 (w, br); 942 (s); 913 (s); 904 (s); 855 (w); 835 (w); 754 (w); 703 (w).

L-Leucine - Initial pH = 1.8. No solid was formed after 18 hours at room temperature. A small quantity of solid was formed after 8.5 hours at 50 °C. Further heating and successive cooling (4 °C) did not increase the amount of product. Then the solvent was completely removed in vacuum at 50 °C and a yellow solid resulted. This solid was washed with water, acetone, diethyl ether and dried under vacuum with P_4O_{10}. Yield: 704 mg (77 %) of $Mo_2O_4(OH)_4(LeuH)$. Anal. Calcd for $C_6H_{17}Mo_2NO_{10}$: C, 15.83; H, 3.76; N, 3.08 %; Found: C, 16.45; H, 3.70; N, 3.01 %. IR (ATR): $\tilde{\upsilon}$/cm^{-1} = 3483 (w, br); 3102 (w, br); 2960 (m); 2871 (w); 1733 (w, br); 1600 (m); 1504 (m); 1470 (w); 1424 (m); 1385 (m); 1365 (m); 1353 (m); 1295 (sh); 1173 (w, br); 1130 (w, br); 941 (s); 914 (sh); 898 (s); 851 (sh); 827 (sh); 764 (w); 747 (w).

L-Methionine - A solid was formed after 25 minutes. Initial pH = 1.8, filtrate pH = 2.5. Yield: 781 mg (82

%) of Mo$_2$O$_4$(OH)$_4$(MetH). Anal. Calcd for C$_5$H$_{15}$Mo$_2$NO$_{10}$S: C, 12.69; H, 3.20; N, 2.96 %; Found: C, 13.38; H, 2.89; N, 3.10 %. IR (ATR): ṽ/cm^{-1} = 3621 (w, br); 3455 (w, br); 3348 (w, br); 3145 (w, br); 3077 (w, br); 3922 (w, br); 1606 (m); 1575 (m); 1503 (m); 1439 (mw); 1427 (m); 1358 (m); 1338 (m); 1333 (m); 1317 (w); 1292 (w); 1280 (w); 1252 (w); 1192 (w); 1148 (mw); 1119 (w); 1102 (w); 1070 (w); 1001 (w); 970 (mw); 940 (s); 913 (s); 893 (s); 877 (m); 764 (mw); 749 (w).

L-Proline - A solid was formed after 25 minutes. Initial pH = 1.8, filtrate pH = 2.4. Yield: 642 mg (73 %) of Mo$_2$O$_4$(OH)$_4$(ProH). Anal. Calcd for C$_5$H$_{13}$Mo$_2$NO$_{10}$: C, 13.68; H, 2.98; Mo, 43.7; N, 3.19 %; Found: C, 14.13; H, 2.85; Mo, 45.8; N, 3.25 %. ^{13}C NMR (CP-MAS solid state): δ/ppm = 176.8 (CO); 175.2 (CO); 173.5 (CO); 65.0 (CH); 61.0 (CH); 49.7 (CH$_2$N); 47.3 (CH$_2$N); 46.9 (CH$_2$N); 30.2 (*CH$_2$*CH); 29.4 (*CH$_2$*CH); 26.2 (*CH$_2$*(CH$_2$)$_2$); 25.8 (*CH$_2$*(CH$_2$)$_2$); 23.7 (*CH$_2$*(CH$_2$)$_2$). IR (ATR): ṽ/cm^{-1} = 3660 (w, br); 3160 (br); 2982 (m); 2891 (w, br); 1611 (m); 1561 (mw); 1473 (w); 1431 (m); 1380 (mw); 1332 (w); 1253 (w); 1168 (w, br); 1088 (w, br); 950 (s); 917 (s); 897 (s); 768 (mw).

N,N-Dimethyl-L-phenylalanine - A solid was formed immediately. Initial pH = 2.0, filtrate pH = 2.4. Yield: 862 mg (83 %) of Mo$_2$O$_4$(OH)$_4$((NMe$_2$)PheH). Anal. Calcd for C$_{11}$H$_{19}$Mo$_2$NO$_{10}$: C, 25.55; H, 3.70; Mo, 38.1; N, 2.71 %; Found: C, 26.25; H, 3.55; Mo, 37.1; N, 2.73 %. IR (ATR and Nujol): ṽ/cm^{-1} = 3551 (br); 3061 (br); 1631 (m); 1494 (w); 1469 (w); 1455 (w); 1428 (sh); 1412 (m); 1351 (m); 1173 (w, br); 1135 (w); 1081 (w); 1043 (w); 947 (s); 917 (s); 905 (sh); 892? (sh); 768 (m); 740 (w); 702 (m); 547 (s, br); 487 (sh); 384 (w).

Section 2.3 - General preparation of Mo$_2$O$_4$(OH)$_4$(aaH) from (NH$_4$)$_6$Mo$_7$O$_{24}$

A stock pH = 1.6 solution with [Mo] = 0.160 was prepared by heating and stirring for several minutes a suspension of (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O (4.67 g, 3.78 mmol Mo$_7$; 26.5 mmol Mo) in 150 mL of water and by adding 15 mL of 1 M HNO$_3$. In a round-bottom flask, 2.00 mmol of amino acid were dissolved in 10 mL of water and pH = 2.0 was obtained by adding 2.0 mL of 1 M HNO$_3$. To this solution, 25.0 mL of the molybdate solution (4.00 mmol of Mo) were added and the resulting colourless solution ([Mo]$_0$ = 0.108) was stirred at room temperature. A colourless solid (Mo$_2$O$_4$(OH)$_4$(aaH)) was obtained after a certain time, depending on the amino acid used. After 20-24 hours, the reaction mixture was filtered. The pH of the solution was measured soon after mixing of the reagents (1-5 min) and after filtration. The solid was washed with acetone, diethyl ether and dried under vacuum with P$_4$O$_{10}$. Details for single preparations are given below.

Glycine - The reaction mixture became opalescent after 5 minutes and a colourless solid was obtained after 4 hours. Initial pH = 1.6, filtrate pH = 2.1. Yield: 734 mg (92 %) of Mo$_2$O$_4$(OH)$_4$(GlyH). ^{13}C NMR

(CP-MAS solid state): δ/ppm = 172.3 (CO); 42.1 (CH$_2$). IR (ATR): $\tilde{\upsilon}$/cm^{-1} = 3574 (w, br); 3429 (sh); 3377 (w, br); 3218 (w, br); 3135 (w, br); 3041 (w, br); 2938 (w, br); 2754 (w, br); 2647 (w, br); 1671 (w); 1622 (m); 1603 (m); 1594 (m); 1575 (m); 1511 (sh); 1504 (sh); 1494 (m); 1490 (m); 1455 (sh); 1446 (m); 1412 (s); 1341 (m); 1148 (w); 1119 (w); 1100 (w); 1052 (w); 1043 (w); 947 (s); 919 (s); 900 (s); 765 (w).

L-Phenylalanine - The reaction mixture became opalescent after 4 hours and a colourless solid was obtained after 22 hours. Initial pH = 1.6, filtrate pH = 2.1. Yield: 841 mg (86 %) of Mo$_2$O$_4$(OH)$_4$(PheH). Anal. Calcd for C$_9$H$_{15}$Mo$_2$NO$_{10}$: Mo 39.2 %; Found: 40.7 %. IR (ATR): $\tilde{\upsilon}$/cm^{-1} = 3525 (w, br); 3029 (w, br); 1605 (m); 1516 (m); 1497 (m); 1454 (w); 1425 (m); 1343 (m); 1246 (w); 1143 (w); 1080 (w, br); 942 (s); 915 (s); 902 (s); 854 (w, br); 765 (w); 753 (w); 703 (w).

L-Methionine - The reaction mixture became opalescent after 30 minutes and a colourless solid was obtained after 4 hours. Initial pH = 1.6, filtrate pH = 2.1. Yield: 855 mg (82 %) of Mo$_2$O$_4$(OH)$_4$(MetH). Anal. Calcd for C$_5$H$_{15}$Mo$_2$NO$_{10}$S: Mo, 40.6 %; Found: 42.5 %. IR (ATR): $\tilde{\upsilon}$/cm^{-1} = 3464 (w, br); 3341 (w, br); 3145 (w, br); 3082 (w, br); 2917 (w, br); 1606 (ms); 1574 (m); 1504 (m); 1439 (m); 1425 (m); 1357 (m); 1332 (m); 1317 (w); 1292 (w); 1279 (w); 1250 (w); 1193 (w); 1148 (mw); 1101 (w); 1068 (w); 1001 (w); 969 (mw); 938 (s); 912 (s); 892 (s); 761 (w); 749 (w).

L-Proline - A solid was formed immediately. Initial pH = 1.6, filtrate pH = 2.1. Yield: 638 mg (73 %) of Mo$_2$O$_4$(OH)$_4$(ProH). Anal. Calcd for C$_5$H$_{13}$Mo$_2$NO$_{10}$: C, 13.68; H, 2.98; Mo, 40.6; N, 3.19 %; Found: C, 14.23; H, 2.83; Mo, 42.5; N, 3.36 %. IR (ATR and Nujol): $\tilde{\upsilon}$/cm^{-1} = 3548 (w, br); 3162 (w, br); 3045 (w, br); 2940 (w, br); 2773 (w, br); 1605 (m); 1557 (m); 1473 (w); 1434 (m); 1393 (mw); 1371 (m); 1337 (m); 1301 (w); 1182 (w); 1039 (w); 945 (s); 914 (s); 900 (s); 766 (m); 544 (s, br); 461 (sh).

N,N-Dimethyl-L-phenylalanine - A solid was formed immediately. Initial pH = 1.6, filtrate pH = 2.1. Yield: 931 mg (90 %) of Mo$_2$O$_4$(OH)$_4$((NMe$_2$)PheH). ^{13}C NMR (CP-MAS solid state): δ/ppm = 171.6 (CO); 140.9 (Ph); 130.8 (Ph); 128.8 (Ph); 127.8 (Ph); 69.9 (CH); 42.0 (NCH$_3$); 36.6 (NCH$_3$); 30.4 (CH$_2$). IR (ATR): $\tilde{\upsilon}$/cm^{-1} = 3560 (w, br); 3052 (w, br); 2737 (w, br); 1628 (m); 1494 (w); 1453 (m); 1432 (m); 1413 (m); 1351 (m); 1178 (w, br); 1081 (w); 1044 (w); 948 (s); 918 (s); 906 (sh); 857 (w); 769 (m); 743 (w); 704 (m).

Section 2.4 - Reactions of glycine and Q$_2$MoO$_4$ (Q = Na or NH$_4$) with different acid concentrations

Reaction at pH = 1 - Compound Na$_2$MoO$_4$·2H$_2$O (971 mg, 4.01 mmol) and glycine (151 mg, 2.00 mmol) were dissolved in 35 mL of water. 65 % HNO$_3$ was added dropwise until pH = 1 and the resulting pale yellow solution ([Mo]$_0$ = 0.108) was stirred at room temperature. The reaction

mixture became opalescent almost immediately and a pale yellow solid was formed after 5 hours. After 24 hours, the solid was collected by filtration, washed with acetone, diethyl ether and dried under vacuum with P_4O_{10}. Yield: 691 mg (86 %) of $(MoO_3)_2(GlyH)(H_2O)_2$. Anal. Calcd for $C_2H_9Mo_2NO_{10}$: Mo, 48.1 %; Found: 47.8 %. IR (ATR): $\tilde{\upsilon}/cm^{-1}$ = 3573 (w, br); 3378 (w, br); 3205 (sh); 3126 (w, br); 3040 (w, br); 2944 (w, br); 1620 (sh); 1615 (sh); 1601 (m); 1547 (m); 1489 (m); 1445 (m); 1410 (ms); 1347 (m); 1307 (w); 1128 (w); 1099 (w); 1041 (w); 947 (s); 927 (s); 917 (s); 894 (s); 767 (w).

The solvent was completely removed from the filtered solution by heating under vacuum. The yellowish residue was identified as $NaNO_3$ (IR spectrum[182]).

This product was also obtained by stirring a suspension of $MoO_3·H_2O$ (1.00 g, 6.19 mmol) and glycine (261 mg, 3.48 mmol) in 20 mL of water under refluxing conditions. The reaction mixture was kept boiling for 5.5 hours and then it was slowly cooled to room temperature. After ca. 16 hours, the colourless solid was collected by filtration then washed with water, acetone and finally dried under vacuum with CaH_2. Yield: 972 mg (79 %) of $(MoO_3)_2(GlyH)(H_2O)_2$.

Reaction at pH = 1, following the procedure of Furuhashi et al.[134] - Compound $(NH_4)_2MoO_4$ (100 mg, 0.51 mmol) was dissolved in 10 mL of water and glycine (21 mg, 0.28 mmol) was dissolved in 3 mL of 1 M HCl. The two solutions were mixed and 6 M HCl was added dropwise until pH = 1. The resulting colourless solution ($[Mo]_0$ = 0.036) was stirred and heated until boiling. A colourless solid was formed before the mixture started to boil (about 20 minutes after mixing). The reaction mixture was kept boiling for 15 minutes and then it was slowly cooled to room temperature. The solid was collected by filtration, washed with 1 M HCl, water, ethanol, diethyl ether and dried under vacuum. Yield: 112 mg (100 %) of $Mo_2O_4(OH)_4(GlyH)$. Anal. Calcd for $C_2H_9Mo_2NO_{10}$: Mo, 48.1 %; Found: 47.5 %; Chloride assay (HNO_3 / $AgNO_3$): negative. IR (ATR and Nujol): $\tilde{\upsilon}/cm^{-1}$ = 3429 (w, br); 3368 (w, br); 3229 (w, br); 3010 (w, br); 2926 (w, br); 2753 (w, br); 2651 (w, br); 2345 (w, br); 2115 (w, br); 1675 (w); 1626 (m); 1592 (m); 1513 (m); 1455 (m); 1414 (m); 1341 (m); 1148 (w); 1118 (w); 1051 (w); 948 (s); 922 (s); 905(s); 761 (w); 529 (s, br); 477 (sh).

Reaction at pH around 0 - Compound $Na_2MoO_4·2H_2O$ (972 mg, 4.01 mmol) and glycine (151 mg, 2.01 mmol) were dissolved in 35 mL of 1 M HNO_3. 65 % HNO_3 was added to keep pH < 1. The resulting pale yellow solution ($[Mo]_0$ = 0.115) was stirred at room temperature. After 5 hours, an opalescence was observed but no solid was formed even after 25 hours. The reaction mixture was concentrated by heating on a water bath at 75 °C for 4 hours and the residual solution was kept at 4 °C for 24 hours. Only a small amount of colourless solid was formed. Finally, the solution was

concentrated up to 5 mL under vacuum and a pale cream solid was formed. The solid was collected by filtration, washed with acetone, diethyl ether and dried under vacuum with P_4O_{10}. Yield: 150 mg of $MoO_3 \cdot nH_2O$ (26 % if MoO_3). IR (ATR): $\tilde{v}/cm^{-1}$ = 3552 (m, br); 3390 (m, br); 3190 (m, br); 1607 (s); 1575 (sh); 1487 (m); 1446 (m); 1411 (s); 1347 (m), 1338 (m); 1110 (w); 1047 (w); 950 (s); 890 (s); 873 (s); 834 (m); 745 (m).

This solid was stirred for 24 hours in 2 mL of water and partially dissolved: only 22 % of it was recovered by filtration. The filtered pH = 4 solution showed a very strong UV absorption at $\lambda <$ 250 nm.

Section 2.5 - Formation of Mo₂O₄(OH)₄(aaH) with excess amino acid

Two aqueous pH = 2 solutions were prepared, one with Q_2MoO_4 (Q = Na or NH_4) and the other with the amount of amino acid necessary to obtain a given M/L molar ratio. The two solutions were mixed in a round-bottom flask and the resulting solution was stirred at room temperature. A colourless or pale yellow solid ($Mo_2O_4(OH)_4(aaH)$) was obtained after a certain time (except when using L-leucine) and the reaction mixture was then filtered. The pH of the solution was measured soon after mixing of the reagents (1-5 min) and after filtration. The solid was washed with acetone, diethyl ether and dried under vacuum with P_4O_{10}. The solvent was completely removed from the filtered solution under vacuum at 40 °C. The resulting solid (identified as impure $[aaH_2]NO_3$) was washed with EtOH, acetone, diethyl ether and finally dried under vacuum with P_4O_{10}. Details for single preparations are given below.

Glycine, M/L = 1 : 2 - The molybdenum solution was prepared with $Na_2MoO_4 \cdot 2H_2O$ (271 mg, 1.12 mmol), 15 mL of water and 1.8 mL of 1 M HNO_3 (pH = 1.8). The amino acid solution was prepared with glycine (169 mg, 2.25 mmol), 15 mL of water and 1.1 mL of 1 M HNO_3 (pH = 2.0). A pale yellow solution resulted after mixing ($[Mo]_0$ = 0.034, pH = 1.8). A pale yellow solid was formed after 10 minutes. The reaction mixture was filtered after 30 minutes (filtrate pH = 1.8). Yield: 174 mg (78 %) of $Mo_2O_4(OH)_4(GlyH)$. Anal. Calcd for $C_2H_9Mo_2NO_{10}$: Mo, 48.1 %; Found: 49.8 %. IR (ATR): $\tilde{v}/cm^{-1}$ = 3565 (w, br); 3528 (w, br); 3381 (w, br); 3306-2400 (br); 1616 (sh); 1599 (m); 1575 (m); 1568 (m); 1489 (m); 1447 (m); 1412 (m); 1341 (m); 1306 (w); 1105 (w); 1041 (w); 944 (s); 914 (s); 892 (s); 765 (w).

A yellow solid (218 mg) was obtained from the filtered solution. This solid was mainly composed of $[GlyH_2]NO_3$, as evidenced by its IR and NMR spectra. IR (ATR): $\tilde{v}/cm^{-1}$ = 3240 (w); 3213 (w); 3023 (sh); 2993 (sh); 2960 (w, br); 2888 (w, br); 2717 (w); 2631 (w); 2430 (w); 1727 (w); 1617 (m); 1585 (m); 1506 (m); 1449 (m); 1354 (s, br); 1235 (m); 1137 (m); 1116 (m); 1039 (m); 937 (m); 915 (w); 890 (m); 871 (w); 828 (m); 814 (w); 647 (m). Readily dissolved in water, giving a solution with pH = 3.8. ^1H NMR (D_2O):

δ/ppm = 3.70 (CH$_2$). ^{13}C{^{1}H} NMR (D$_2$O): δ/ppm = 172.5 (CO); 41.5 (CH$_2$).

Glycine, M/L = 1 : 13.7 - The molybdenum solution was prepared with Na$_2$MoO$_4$·2H$_2$O (279 mg, 1.15 mmol), 3 mL of water and 3 mL of 1 M HNO$_3$ (pH = 1.8). The amino acid solution was prepared with glycine (1.19 g, 15.8 mmol), 89 mL of water and 8.2 mL of 1 M HNO$_3$ (pH = 2.0). A pale yellow solution resulted after mixing ([Mo]$_0$ = 0.011 , pH = 1.8). An opalescence was observed after 5 minutes and successively a pale yellow solid was formed. The reaction mixture was filtered after 16 hours (filtrate pH = 1.8). Yield: 161.4 mg (70 %) of Mo$_2$O$_4$(OH)$_4$(GlyH). IR (ATR): ṽ/cm^{-1} = 3576 (w); 3431 (w); 3385 (w); 3213 (w); 2943 (w); 1675 (w); 1622 (m); 1592 (m); 1511 (m); 1455 (m); 1412 (m); 1341 (m); 1148 (w); 1118 (w); 1101 (w); 948 (s); 919 (s); 903 (s); 764 (w).

A yellow solid was obtained from the filtered solution. This solid is mainly composed of [GlyH$_2$]NO$_3$, as evidenced by its IR spectrum. IR (ATR): ṽ/cm^{-1} = 3995 (w); 3936 (w); 3923 (w); 3905 (w); 3873 (w); 3852 (w); 3836 (w); 3824 (w); 3800 (w); 3763 (w); 3736 (w); 3724 (w); 3711 (w); 3446 (w); 3206 (m); 3156 (w); 2964 (m); 2906 (m); 2837 (m); 746 (m); 2720 (m); 2640 (m); 2541 (m); 2441 (w); 1724 (s); 1624 (m); 1595 (m); 1517 (m); 1442 (m); 1407 (s); 1354 (s); 1329 (s); 1212 (s); 1121 (s); 1042 (s); 936 (m); 914 (s); 890 (s); 867 (s); 829 (m); 813 (s); 738 (m); 711 (w); 662 (m).

L-Phenylalanine, M/L = 1 : 2 - The molybdenum solution was prepared with Na$_2$MoO$_4$·2H$_2$O (415 mg, 1.71 mmol), 10 mL of water and 1.8 mL of 1 M HNO$_3$ (pH = 1.8). The amino acid solution was prepared with L-phenylalanine (566 mg mg, 3.42 mmol), 10 mL of water and 3.4 mL of 1 M HNO$_3$ (pH = 2.2). A pale yellow solution resulted after mixing ([Mo]$_0$ = 0.068, pH = 2.0). A pale yellow solid was formed after 3 hours. The reaction mixture was filtered after 48 hours (filtrate pH = 2.0). Yield: 349 mg (84 %) of Mo$_2$O$_4$(OH)$_4$(PheH). Anal. Calcd for C$_9$H$_{15}$Mo$_2$NO$_{10}$: Mo, 39.2 %; Found: 40.5 %. IR (ATR): ṽ/cm^{-1} = 3579 (w, br); 3487 (w, br); 3032 (w, br); 1605 (m); 1514 (m); 1497 (m); 1455 (w); 1421 (m); 1343 (m); 1244 (w); 1139 (w); 1078 (w, br); 942 (s); 915 (s); 900 (s); 856 (sh); 766 (sh); 753 (w); 701 (w).

A pale yellow solid (162 mg) was obtained from the filtered solution. This solid is mainly composed of [PheH$_2$]NO$_3$, as evidenced by IR spectrum. IR (ATR): ṽ/cm^{-1} = 3530 (w, br); 3055 (m, br); 1711 (m); 1670 (m); 1607 (m); 1583 (sh); 1496 (m); 1454 (m); 1445 (m); 1422 (m); 1361 (s, br); 1344 (s); 1206 (m); 1135 (m); 1083 (w); 943 (s); 922 (s); 908 (s); 874 (m); 854 (w); 836 (w); 823 (w); 810 (w); 797 (w); 759 (m); 746 (s); 698 (s).

L-Leucine, M/L = 1 : 2 - The molybdenum solution was prepared with Na$_2$MoO$_4$·2H$_2$O (358 mg, 1.48 mmol), 10 mL of water and 2 mL of 1 M HNO$_3$ (pH = 2.0). The amino acid solution was prepared with L-leucine (388 mg, 2.96 mmol), 10 mL of water and 3 mL of 1 M HNO$_3$ (pH = 2.0). A pale yellow solution resulted after mixing ([Mo]$_0$ = 0.059, pH = 1.8). The reaction mixture was stirred and heated at 50 °C and a colourless solid was formed after 3.5 hours. The reaction mixture was then stirred at room temperature and filtered after 3 days. Yield: 312 mg (93 %) of Mo$_2$O$_4$(OH)$_4$(LeuH). Anal. Calcd for C$_6$H$_{17}$Mo$_2$NO$_{10}$: Mo, 42.2

%; Found: 42.7 %. IR (ATR): $\tilde{\upsilon}/cm^{-1}$ = 3700-3320 (br); 3320-2700 (br); 2963 (w); 2871 (w); 1718 (w); 1621 (m); 1604 (m); 1507 (m); 1426 (m); 1385 (m); 1365 (m); 1350 (m); 1297 (w); 1214 (w); 1172 (w, br); 1131 (w, br); 1036 (w, br); 942 (s); 915 (sh); 902 (s); 822 (w); 767 (w); 749 (sh).

The pale yellow filtered solution was concentrated up to 5 mL under vacuum (40 °C) and left evaporating at room temperature. Colourless needle-shaped crystals of [LeuH$_2$]NO$_3$ were obtained in 24 hours. IR (ATR): $\tilde{\upsilon}/cm^{-1}$ = 3225 (w, br); 3191 (w, br); 3044 (w, br); 2975 (m); 2958 (m); 2868 (m); 1718 (s); 1625 (w); 1579 (w); 1509 (m); 1474 (w); 1454 (m); 1414 (s); 1385 (m); 1345 (s); 1325 (s); 1262 (m); 1214 (s); 1170 (s); 1143 (m); 1075 (m); 1035 (m); 995 (m); 961 (w); 939 (m); 912 (m); 835 (w); 806 (m); 753 (w); 730 (w); 711 (w). Readily dissolved in water, giving a solution with pH = 2.2. ^{1}H NMR (D$_2$O): δ/ppm = 3.98 (m, 1.0H, CHN); 1.80 (m, 1.0H, CHMe$_2$); 1.70 (m, 2.0H, CH$_2$); 0.91 (t, $^3J_{HH}$ = 5.5 Hz, 6.2H, CH$_3$). ^{13}C{^{1}H} NMR (D$_2$O): δ/ppm = 173.1 (CO); 51.7 (CHN); 39.0 (CH$_2$); 24.0 (CHMe$_2$); 21.6 (CH$_3$); 20.9 (CH$_3$).

L-Leucine, M/L = 1 : 1 - The molybdenum solution was prepared with Na$_2$MoO$_4$·2H$_2$O (358 mg, 1.48 mmol), 10 mL of water and 2 mL of 1 M HNO$_3$ (pH = 2.0). The amino acid solution was prepared with L-leucine (195 mg, 1.48 mmol), 10 mL of water and 1.5 mL of 1 M HNO$_3$ (pH = 2.0). A pale yellow solution resulted after mixing ([Mo]$_0$ = 0.063, pH = 1.8). The reaction mixture was stirred at 50 °C for 3.5 hours and then at room temperature for 3 days. Since no solid was formed under these conditions, the reaction mixture was concentrated up to 14 mL under vacuum (35 °C). Subsequently, a pale yellow solid was obtained and the reaction mixture was filtered. Yield: 249 mg (74 %) of Mo$_2$O$_4$(OH)$_4$(LeuH). Anal. Calcd for C$_6$H$_{17}$Mo$_2$NO$_{10}$: Mo, 42.2 %; Found: 43.2 %. IR (ATR): $\tilde{\upsilon}/cm^{-1}$ = 3700-3320 (br); 3320-2700 (br); 2963 (w); 2871 (w); 1718 (w); 1621 (m); 1604 (m); 1507 (m); 1426 (m); 1385 (m); 1365 (m); 1350 (m); 1297 (w); 1214 (w); 1172 (w, br); 1131 (w, br); 1036 (w, br); 942 (s); 915 (sh); 902 (s); 822 (w); 767 (w); 749 (sh).

L-Methionine, M/L = 1 : 2 - The molybdenum solution was prepared with (NH$_4$)$_2$MoO$_4$ (301 mg, 1.53 mmol), 20 mL of water and 3 M HNO$_3$ until pH = 2. The amino acid solution was prepared with L-methionine (458 mg, 3.07 mmol), 20 mL of water and 3 M HNO$_3$ until pH = 2. A colourless solution resulted after mixing ([Mo]$_0$ = 0.034, pH = 2.0). A colourless solid was formed after 30 minutes. The reaction mixture was filtered after 15 hours. Yield: 269 mg (74 %) of Mo$_2$O$_4$(OH)$_4$(MetH). Anal. Calcd for C$_5$H$_{15}$Mo$_2$NO$_{10}$S: C, 12.69; H, 3.20; N, 2.96 %; Found: C, 13.25; H, 2.75; N, 2.88 %. ^{13}C NMR (CP-MAS solid state): δ/ppm = 174.4 (CO); 171.8 (CO); 54.7 (CH); 31.5 (CH$_2$CH); 30.6 (CH$_2$CH); 28.7 (SCH$_2$); 15.3 (SCH$_3$); 14.3 (SCH$_3$); 12.4 (SCH$_3$). IR (ATR and Nujol): $\tilde{\upsilon}/cm^{-1}$ = 3680-3280 (br); 3145 (w, br); 3065 (w, br); 2920 (w, br); 2861 (sh); 1604 (m); 1570 (sh); 1501 (m); 1443 (sh); 1425 (m); 1357 (mw); 1334 (m); 1318 (w); 1290 (w); 1279 (w); 1251 (w); 1195 (w); 1150 (w); 1103 (w); 1070 (w); 1000 (w); 944 (s); 914 (s); 895 (s); 761 (mw); 541 (s, br).

A colourless solid was obtained from the filtered solution. This solid was stirred with 2 mL of water and the resulting suspension was filtered. The colourless solid obtained (L-Methionine) was washed with

ethanol, acetone, diethyl ether and finally dried under vacuum with P_4O_{10}. IR (ATR): $\tilde{v}/cm^{-1}$ = 3148 (w, br); 2984 (sh); 2951 (sh); 2915 (m, br); 2734 (w, br); 2630 (w, br); 2566 (w, br); 2110 (w, br); 1608 (s); 1581 (s); 1563 (s); 1558 (s); 1506 (s); 1447 (m); 1405 (s); 1351 (s); 1329 (sh); 1316 (s); 1276 (mw); 1241 (ms); 1185 (w); 1150 (m); 1119 (w); 1068 (w); 1024 (w); 1004 (sh); 979 (m); 951 (w); 873 (mw); 803 (w); 766 (w); 750 (w); 720 (w); 707 (w); 681 (w); 656 (w).

L-Proline, M/L = 1 : 2 - The molybdenum solution was prepared with $(NH_4)_2MoO_4$ (307 mg, 1.57 mmol), 40 mL of water and 3 M HNO_3 until pH = 2. The amino acid solution was prepared with L-methionine (361 mg, 3.07 mmol), 40 mL of water and 3 M HNO_3 until pH = 2. A colourless solution resulted after mixing ($[Mo]_0$ = 0.019, pH = 2.0). A colourless solid was formed after 5 minutes. The reaction mixture was filtered after 1.5 hours. Yield: 233 mg (68 %) of $Mo_2O_4(OH)_4(ProH)$. Anal. Calcd for $C_5H_{13}Mo_2NO_{10}$: C, 13.68; H, 2.98; N, 3.19 %; Found: C, 13.99; H, 2.29; N, 3.44 %. ^{13}C NMR (CP-MAS solid state): δ/ppm = 175.0 (CO); 62.4 (CH); 61.6 (CH); 47.9 (CH_2N); 45.8 (CH_2N); 29.5 (CH_2CH); 28.7 (CH_2CH); 25.3 ($CH_2(CH_2)_2$); 24.6 ($CH_2(CH_2)_2$). IR (ATR and Nujol): $\tilde{v}/cm^{-1}$ = 3562 (w,br), 3159 (w, br); 3021 (w, br); 1607 (m); 1429 (m); 1370 (m); 1335 (m); 1180 (w, br); 1040 (w, br); 946 (s); 920 (s); 903 (s); 768 (w); 615 (sh), 561 (s, br).

In order to get single crystals, L-methionine and L-proline reactions were also carried out under the same experimental conditions, but with slow reactant mixing. In a 9 mL test tube, 2 mL of a $(NH_4)_2MoO_4$ solution were layered with 4.5 mL of water which in turn were layered with 1.5 mL of the amino acid solution. The molybdenum and amino acid solutions were prepared with a molar ratio M/L = 1 : 2 and an amount of $(NH_4)_2MoO_4$ that would give, for complete mixing, a 0.034 M solution in the total 8.0 mL volume. The amount of HNO_3 added in both solutions was enough to give, for complete mixing, a pH = 2 solution in the total 8.0 mL volume. After 3 days, a colourless solid was formed. The powder obtained in both cases corresponded to $Mo_2O_4(OH)_4(aaH)$.

Section 2.6 - Formation of Mo₂O₄(OH)₄(aaH) with a distinct thermal treatment

Compound Q_2MoO_4 (Q = Na or NH_4) was dissolved in water and 3 M HNO_3 was added dropwise until pH = 2.0. A double molar amount of amino acid was dissolved in water and 3 M HNO_3 was added dropwise until pH = 2.0. The two solutions were mixed in a round-bottom flask and the resulting colourless solution was stirred at room temperature or heated. A colourless solid $(Mo_2O_4(OH)_4(aaH))$ was subsequently obtained. The reaction mixture was filtered and the solid was washed with water, ethanol, acetone, diethyl ether and dried under vacuum with P_4O_{10}. Details for single preparations are given below.

L-Phenylalanine, RT - The pH = 2 molybdenum solution was prepared with $(NH_4)_2MoO_4$ (112 mg, 0.57 mmol) in 10 mL of water. The pH = 2 amino acid solution was prepared with L-phenylalanine (188 mg, 1.14 mmol) in 5 mL of water. The reaction mixture ($[Mo]_0 = 0.038$) was stirred at room temperature. A colourless solid was formed after 2 hours. The reaction mixture was filtered after 24 hours. Yield: 136 mg (97 %) of $Mo_2O_4(OH)_4(PheH)$. Anal. Calcd for $C_9H_{15}Mo_2NO_{10}$: C, 22.10; H, 3.09; N, 2.86 %; Found: C, 23.05; H, 2.64; N, 2.86 %. ^{13}C NMR (CP-MAS solid state): δ/ppm = 172.6 (CO); 134.6 (Ph); 132.4 (Ph); 130.7 (Ph); 129.4 (Ph); 57.3 (CH); 35.7 (CH_2). IR (ATR and Nujol): $\tilde{v}$/cm^{-1} = 3574 (w); 3463 (w, br); 3200-3000 (w, br), 2804 (w, br), 2540 (w, br), 1621 (m); 1587 (m); 1499 (m); 1475 (m); 1454 (m); 1443 (m); 1418 (ms); 1343 (m); 1263 (w); 1238 (w); 1209 (w); 1129 (w); 1099 (w); 1086 (w); 1068 (w); 1031 (w); 940 (s); 913 (s); 894 (s); 768 (sh); 752 (m); 704 (m); 534 (s, br).

L-Phenylalanine, 70 °C - The pH = 2 molybdenum solution was prepared with $(NH_4)_2MoO_4$ (300 mg, 1.53 mmol) in 20 mL of water. The pH = 2 amino acid solution was prepared with L-phenylalanine (505 mg, 3.05 mmol) in 20 mL of water. The reaction mixture ($[Mo]_0 = 0.038$) was stirred at 70 °C. A colourless solid was formed after 1.5 hours. After 2 hours, the reaction mixture was cooled to room temperature and filtered. Yield: 380 mg (101 %) of $Mo_2O_4(OH)_4(PheH)$. ^{13}C NMR (CP-MAS solid state): δ/ppm = 172.6 (CO); 134.5 (Ph); 133.6 (Ph); 132.5 (Ph); 129.6 (Ph); 57.3 (CH); 35.6 (CH_2). IR (ATR and Nujol): $\tilde{v}$/cm^{-1} = 3584 (w, br); 3499 (w, br); 3028 (w, br); 1607 (m, br); 1514 (w); 1495 (w); 1454 (w); 1426 (m); 1345 (w); 1244 (w); 1132 (w, br); 943 (s); 916 (s); 903 (s); 766 (sh); 754 (mw); 704 (w); 533 (s, br).

L-Leucine, RT / 70 °C / 4 °C - The pH = 2 molybdenum solution was prepared with $(NH_4)_2MoO_4$ (303 mg, 1.55 mmol) in 20 mL of water. The pH = 2 amino acid solution was prepared with L-leucine (405 mg, 3.09 mmol) in 20 mL of water. The reaction mixture ($[Mo]_0 = 0.039$) was stirred at room temperature for 19 hours, then at 70 °C for 2 hours and finally kept at 4 °C for 17 hours. In none of these conditions, a solid was formed. Thereafter, the solution was concentrated up to 10 mL under vacuum. A colourless solid was formed and the reaction mixture was filtered. Yield: 221 mg (63 %) of $Mo_2O_4(OH)_4(LeuH)$. Anal. Calcd for $C_6H_{17}Mo_2NO_{10}$: C, 15.83; H, 3.76; N, 3.08 %; Found: C, 16.80; H, 3.40; N, 3.20 %. ^{13}C NMR (CP-MAS solid state): δ/ppm = 173.2 (CO); 53.2 (CHN); 39.2 (CH_2); 25.1 ($CHMe_2$); 21.3 (CH_3); 20.1 (CH_3). IR (ATR and Nujol): $\tilde{v}$/cm^{-1} = 3600-3300 (w, br); 3300-2500 (w, br); 2958 (w); 2929 (sh); 2871 (w); 1623(sh); 1732 (w, br); 1622 (sh); 1599 (m); 1505 (m,br); 1470 (sh); 1427 (m); 1388 (w); 1369 (w), 1349 (m); 1171 (w); 1132 (w); 1122 (w); 1061 (w, br); 939 (s); 916 (sh); 896 (s); 767 (m); 747 (sh); 537 (s, br).

L-Leucine, RT / 80 °C / 4 °C - The pH = 2 molybdenum solution was prepared with $Na_2MoO_4 \cdot 2H_2O$ (207 mg, 0.85 mmol) in 10 mL of water. The pH = 2 amino acid solution was prepared with L-leucine (225 mg, 1.72 mmol) in 10 mL of water. The reaction mixture ($[Mo]_0 = 0.042$, pH = 1.8) was stirred at room temperature for 28 hours, then at 80 °C for 2 hours and finally kept at 4 °C for 10 hours. In none of these conditions, a solid was formed (pH = 1.8). Therefore, the solution was concentrated up to a few mL under

vacuum. A colourless solid was formed and the reaction mixture was filtered. Yield: 177 mg (91 %) of Mo$_2$O$_4$(OH)$_4$(LeuH). IR (ATR): $\tilde{\upsilon}$/cm^{-1} = 3700-3320 (br); 3320-2700 (br); 2958 (w); 2871 (w); 1731 (w, br); 1621 (m); 1597 (sh); 1505 (m); 1482 (m); 1426 (m); 1389 (w); 1369 (w); 1350 (m); 1336 (w); 1297 (w); 1263 (w); 1176 (w, br); 1135 (w); 1118 (w); 1064 (w, br); 940 (s); 912 (sh); 900 (s); 848 (w); 767 (w); 749 (sh).

Section 2.7 - Formation of Mo$_2$O$_4$(OH)$_4$(aaH) in D$_2$O

The amino acid (PheH, LeuH, ProH, (NMe$_2$)PheH) was dissolved in D$_2$O and 3 M HNO$_3$ was added dropwise until pH = 2. Then a half-molar amount of (NH$_4$)$_2$MoO$_4$ and dropwise 3 M HNO$_3$ until pH = 2 were added. The resulting colourless solution (M/L = 1 : 2, [Mo]$_0$ ≈ 0.08) was stirred at room temperature. A colourless solid was formed almost immediately (PheH, ProH, (NMe$_2$)PheH) or after 1 hour (LeuH). The solid (except for PheH) was collected by filtration, washed with water, ethanol, acetone, diethyl ether and finally dried under vacuum with P$_4$O$_{10}$. The ^{1}H and ^{13}C NMR spectra of the following solutions were recorded:

- The pH = 2 amino acid solution (only for LeuH and ProH)

- The reaction mixture before the formation of Mo$_2$O$_4$(OH)$_4$(aaH) (only for LeuH)

- The reaction mixture, at various time intervals after the formation of Mo$_2$O$_4$(OH)$_4$(aaH)

Details for single reactions are given below. Only one ^{1}H and ^{13}C spectrum is reported for each amino acid since they were similar.

L-Phenylalanine - The pH = 1.8 amino acid solution was prepared with L-phenylalanine (34 mg, 0.20 mmol) in 1.0 mL of D$_2$O. Nitric acid and (NH$_4$)$_2$MoO$_4$ (20 mg, 0.10 mmol) were added and a solid was immediately formed. The ^{1}H and ^{13}C NMR spectra were recorded after a few minutes and after 40 hours.
^{1}H NMR (D$_2$O): δ/ppm = 7.38-7.26 (m, 5.0H, Ph); 7.08 (I = 1 triplet, ^{1}J$_{N-H}$ = 52.3 Hz, ND$_3$H$^+$); 4.23 (multiplet ABX pattern, 1.0H, CH); 3.28 (multiplet ABX pattern, 1.0H, C*H*H'); 3.14 (multiplet ABX pattern, 1.0H, CH*H'*). ^{13}C{^{1}H} NMR (D$_2$O): δ/ppm = 171.9 (CO) ; 134.2 (Ph); 129.4 (Ph); 129.2 (Ph); 128.0 (Ph); 54.5 (CH); 35.7 (CH$_2$).

L-Leucine - The pH = 2.0 amino acid solution was prepared with L-leucine (134 mg, 1.02 mmol) in 5 mL of H$_2$O / D$_2$O. Nitric acid and (NH$_4$)$_2$MoO$_4$ (100 mg, 0.51 mmol) were added and a solid was formed after 1 hour. The ^{1}H and ^{13}C NMR spectra were recorded soon after reactant mixing, thus before the formation of Mo$_2$O$_4$(OH)$_4$(LeuH), and after 40 hours. ^{1}H NMR (D$_2$O): δ/ppm = 7.05 (I = 1 triplet, ^{1}J$_{N-H}$ = 52.6 Hz, ND$_3$H$^+$); 3.97 (multiplet ABX pattern, 1.0H, CHN); 1.79 (m, 1.0H, CHMe$_2$); 1.68 (m, 2.0H, CH$_2$); 0.89 (t, ^{3}J$_{H-H}$ = 5.5 Hz, 6.0H, CH$_3$). ^{13}C{^{1}H} NMR (D$_2$O): δ/ppm = 173.2 (CO); 51.8 (CHN); 39.0 (CH$_2$); 24.0

(CHMe$_2$); 21.7 (CH$_3$); 20.9 (CH$_3$). Yield: 111 mg (96 %) of Mo$_2$O$_4$(OH)$_4$(LeuH). IR (ATR): $\tilde{v}$/cm^{-1} = 3700-3300 (w, br); 3300-2600 (w, br); 2958 (w); 2868 (w); 1621 (m); 1604 (sh); 1506 (m); 1485 (m); 1426 (m); 1350 (m); 1172 (w); 1132 (w); 1168 (w, br); 940 (s); 913 (sh); 899 (s); 768 (w); 750 (sh).

L-Proline - The pH = 2 amino acid solution was prepared with L-proline (36 mg, 0.31 mmol) in 0.6 mL of D$_2$O. Nitric acid and (NH$_4$)$_2$MoO$_4$ (30 mg, 0.15 mmol) were added and a solid was immediately formed. The ^{1}H and ^{13}C NMR spectra were recorded after 40 minutes, 20 hours and 92 hours. ^{1}H NMR (D$_2$O): δ/ppm = 7.07 (I = 1 triplet, $^1J_{N-H}$ = 52.7 Hz, ND$_3$H$^+$); 4.22 (multiplet ABX pattern, 1.0H, CH); 3.36 and 3.30 (overlapping m, 2.1H, CH$_2$N); 2.32 (multiplet ABX pattern, 1.0H, C*H*H'CH); 2.06 (multiplet ABX pattern, 1.0H, CH*H'*CH); 1.97 (m, 2.0H, C*H$_2$*(CH$_2$)$_2$). ^{13}C{^{1}H} NMR (D$_2$O): δ/ppm = 173.1 (CO); 60.3 (CH); 46.2 (CH$_2$N); 28.6 (*C*H$_2$CH); 23.5 (*C*H$_2$(CH$_2$)$_2$). Yield: 15 mg (45 %) of Mo$_2$O$_4$(OH)$_4$(ProH) - additional colourless solid was formed in the NMR tube after 4 days. IR (ATR): $\tilde{v}$/cm^{-1} = 3548 (w, br); 3165 (w, br); 3038 (w, br); 1606 (m); 1561 (sh); 1473 (w); 1433 (m), 1397 (w); 1372 (w); 1336 (w);1174 (w); 1044 (w); 946 (s); 916 (s); 902 (s); 768 (mw).

N,N-Dimethyl-L-phenylalanine - The pH = 1.8 amino acid solution was prepared with *N,N*-dimethyl-L-phenylalanine (79 mg, 0.40 mmol) in 2.0 mL of D$_2$O. Nitric acid and (NH$_4$)$_2$MoO$_4$ (40 mg, 0.20 mmol) were added and a solid was immediately formed. The ^{1}H and ^{13}C NMR spectra were recorded after 4 days. ^{1}H NMR (D$_2$O, filtered solution): δ/ppm = 7.35-7.25 (m, 5.0H, C$_6$H$_5$); 7.05 (I = 1 triplet, $^1J_{N-H}$ = 52.4 Hz, ND$_3$H$^+$); 4.09 (multiplet ABX pattern, 0.9H, CH); 3.33 (multiplet ABX pattern, 0.9H, C*H*H'); 3.13 (multiplet ABX pattern, 0.9H, CH*H'*); 2.92 and 2.88 (superimposed s, 6.0H, NCH$_3$). ^{13}C{^{1}H} NMR (D$_2$O, filtered solution): δ/ppm = 170.5 (CO); 134.4 (Ph); 129.2 (Ph); 129.1 (Ph); 127.8 (Ph); 69.7 (CH); 42.6 (NCH$_3$); 40.6 (NCH$_3$); 33.3 (CH$_2$). Yield: 40 mg (77 %) of Mo$_2$O$_4$(OH)$_4$((NMe$_2$)PheH) - Additional solid was formed in NMR tube after 5 days. Anal. Calcd for C$_{11}$H$_{19}$Mo$_2$NO$_{10}$: C, 25.55; H, 3.70; N, 2.71 %; Found: C, 26.69; H, 3.25; N, 2.75 %. ^{13}C NMR (CP-MAS solid state): δ/ppm = 171.6 (CO); 140.8 (Ph); 130.5 (Ph); 128.8 (Ph); 127.7 (Ph); 68.9 (CH); 41.8 (NCH$_3$); 37.2 (NCH$_3$); 30.3 (CH$_2$). IR (ATR and Nujol): $\tilde{v}$/cm^{-1} = 3536 (w, br); 3055 (w, br); 3023 (w); 2963 (w); 2731 (w, br); 1625 (m); 1583 (sh); 1494 (w); 1470 (sh); 1455 (sh); 1431 (sh); 1411 (m, br); 1351 (m); 1259 (w); 1172 (w, br); 1138 (w); 1081 (w); 1045 (w); 945 (s); 916 (s); 906 (s); 803(w); 768 (m); 756 (sh); 742 (w); 703 (m); 541 (s, br); 482 (sh); 384 (w).

Section 2.8 - Reactions between L-leucine and (NH$_4$)$_6$Mo$_7$O$_{24}$

M/L = 2 : 1, room temperature - A reaction mixture consisting of (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O (707 mg, 4.00 mmol Mo), L-leucine (263 mg, 2.00 mmol), 32.7 mL of water and 4.3 mL of 1 M HNO$_3$ was stirred at room temperature ([Mo]$_0$ = 0.108, pH = 1.8). The initially colourless solution became light blue after 1 hour, blue after 4 hours and dark blue after 22 hours. This solution was heated at

50 °C in an open vessel for 4.5 hours and some solid was formed. The reaction mixture was filtered and a pale light-blue solid was obtained. The solid was washed with acetone, diethyl ether (it became colourless) and dried under vacuum with P_4O_{10}. Yield: 234 mg (26 %) of $Mo_2O_4(OH)_4(LeuH)$. IR (ATR): $\tilde{v}/cm^{-1}$ = 3398 (m, br); 3243 (m, br); 2960 (m); 2871 (w); 1627 (sh); 1601 (s); 1514 (m); 1470 (w); 1427 (m); 1387 (w); 1365 (m); 1350 (m); 1320 (w); 1296 (w); 1179 (w); 1168 (w); 1135 (w); 941 (s); 914 (sh); 898 (s); 853 (sh); 826 (sh); 766 (w); 749 (w).

GC-MS qualitative analysis of the dark blue filtered solution (pH = 2.4) revealed the presence of CO_2 and 3-methylbutyronitrile. The filtered solution was mixed with the light blue-green organic solution used for washings and gently heated on a water bath. After a few minutes, the blue colour disappeared and a pale yellow solution resulted.[g] When the solution volume was reduced up to 9 mL, a yellow solid was formed. After filtration, the solid was washed with acetone and changed colour to pale green-blue. Another part of this solid was collected by concentrating the filtered solution and by washing the pale yellow solid obtained with acetone. Yield: 208 mg of a pale blue-green solid. IR (ATR): $\tilde{v}/cm^{-1}$ = 3427 (m, br); 3197 (m, br); 2969 (m, br); 1613 (m); 1498 (w); 1425 (m); 1348 (w); 1182 (w, br); 1133 (w, br); 976 (w); 950 (m); 928 (m); 871 (s); 764 (m, br); 689 (m).

M/L = 1 : 2, room temperature - A reaction mixture consisting of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (272 mg, 1.54 mmol Mo), L-leucine (404 mg, 3.08 mmol), 20 mL of water and 2.7 ml of 1 M HNO_3 was stirred at room temperature ($[Mo]_0$ = 0.068, pH = 2.0). After 2 hours, a colourless solid was formed and the solution became pale light blue. The solid was collected by filtration, washed with water, ethanol, acetone and diethyl ether and dried under vacuum with P_4O_{10}. Filtrate pH = 2.0. Yield: 77 mg (22 %) of $Mo_2O_4(OH)_4(LeuH)$. IR (ATR): $\tilde{v}/cm^{-1}$ = 3700-3320 (br); 3320-2700 (br); 2958 (w); 2871 (w); 1731 (w, br); 1621 (m); 1597 (sh); 1505 (m); 1482 (m); 1426 (m); 1389 (w); 1369 (w); 1350 (m); 1336 (w); 1297 (w); 1263 (w); 1176 (w, br); 1135 (w); 1118 (w); 1064 (w, br); 940 (s); 912 (sh); 900 (s); 848 (w); 767 (w); 749 (sh).

M/L = 2 : 1, reflux conditions - A reaction mixture consisting of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (803 mg, 4.54 mmol Mo), L-leucine (298 mg, 2.27 mmol), 30 mL of water and 4.5 ml of 1 M HNO_3 was stirred and heated under refluxing conditions ($[Mo]_0$ = 0.131, pH = 1.8). After 2 hours, a colourless solid was formed and after 3 hours the reaction mixture was cooled to room temperature and filtered. The colourless solid was washed with acetone and dried under vacuum with CaH_2.

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g The colour change from faint yellow to blue and again to faint yellow indicates the redox behaviour of molybdenum centre.[173] The blue colour is typical of mixed valence Mo(VI) and Mo(V), well known as *molybdenum blue*.[1]

Yield: 429 mg (58 %) of $MoO_3 \cdot H_2O$. IR (ATR and Nujol): $\tilde{\upsilon}/cm^{-1}$ = 3600-3300 (w, br); 3215 (w); 3016 (w); 1608 (w); 1438 (m); 1420 (m); 971 (m); 894 (s); 874 (s); 704 (w); 580 (sh); 519 (s, br); 372 (mw).

The filtered solution (pH = 2.4) was concentrated up to a few mL and a colourless solid was formed. This solid was collected by filtration, washed with acetone and dried under vacuum with CaH_2. Yield: 122 mg of a mixture of $Mo_2O_4(OH)_4(LeuH)$ and $[LeuH_2]NO_3$. IR (ATR and Nujol): $\tilde{\upsilon}/cm^{-1}$ = 3650-3300 (w, br); 3204 (w, br); 3039 (w); 2959 (w); 1716 (mw); 1622 (m); 1605 (m); 1507 (m); 1411 (m); 1385 (m); 1347 (m); 1321 (m); 1218 (m); 1169 (m); 1143 (m); 1074 (w); 1036 (w); 972 (sh); 939 (m); 895 (s, br); 825 (w); 805 (w); 766 (w); 744 (w); 710 (w); 578 (sh); 536 (s, br); 372 (w).

Section 2.9 - Formation of $Mo_2O_4(OH)_4(GlyH)$: pH vs. time measurements

The following solutions were prepared:

- Solution *A*: 200 mL of 0.194 M NaOH, titrated with potassium hydrogen phthalate

- Solution *B*: 200 mL of 1.084 M HNO_3, titrated with solution *A*.

- Solution *C*: 100 mL of 0.163 M glycine with pH = 2.00, prepared with 1.22 g (16.3 mmol) of glycine, 8.5 mL of solution *B* and water until 100 mL of volume.

- Solution *D*: 100 mL of 0.163 M molybdate with pH = 2.00, prepared with 3.948 g (16.31 mmol) of $Na_2MoO_4 \cdot 2H_2O$, 20 mL of solution *B* and water until 100 mL of volume.

Reactions **I-VI** (described below) were carried out in a 100 mL beaker with simultaneous measurement of pH as a function of time with the glass pH-electrode. Plotted data are reported in section 3.2. The products obtained from reactions **I**, **II**, **III**, **IV**, **V-2** and **VI** were identified as $Mo_2O_4(OH)_4(GlyH)$ from their ATR spectra (not reported).

Reaction **I** - 12.3 mL of solution *C* (2.00 mmol of glycine), 12.3 mL of solution *D* (2.00 mmol of Mo) and 15.4 mL of water were mixed and stirred at room temperature. Initial concentrations, for a 40.0 mL total volume, were $5.00 \cdot 10^{-2}$ M for molybdenum and $5.00 \cdot 10^{-2}$ M for glycine. After 12 minutes the reaction mixture became opalescent and after 25 minutes a colourless solid was formed. After 101 minutes, the reaction mixture was filtered (final pH = 2.17). The solid was washed with water, then dried under vacuum with CaH_2. Yield: 333 mg (84 %) of $Mo_2O_4(OH)_4(GlyH)$.

Reaction **II** - 12.5 mL of solution *C* (2.04 mmol of glycine), 20.0 mL of solution *D* (3.26 mmol of Mo) and 15.4 mL of water were mixed and stirred at room temperature. Initial concentrations, for a 32.5 mL total volume, were $1.00 \cdot 10^{-1}$ M for molybdenum and $6.27 \cdot 10^{-2}$ M for glycine. After 14 minutes the reaction mixture became opalescent and after 31 minutes a colourless solid was formed. After 191 minutes, the reaction mixture was filtered (final pH = 2.48). The solid was washed with water, then dried under vacuum with CaH_2. Yield: 575 mg (88 %) of $Mo_2O_4(OH)_4(GlyH)$.

Reaction **III** - 7.6 mL of solution *C* (1.25 mmol of glycine), 15.3 mL of solution *D* (2.50 mmol of Mo) and 14.6 mL of water were mixed and stirred at room temperature. Initial concentrations, for a 37.5 mL total volume, were $6.66 \cdot 10^{-2}$ M for molybdenum and $3.34 \cdot 10^{-2}$ M for glycine. After 29 minutes the reaction mixture became opalescent and after 46 minutes a colourless solid was formed. After 141 minutes, the reaction mixture was filtered (final pH = 2.36). The solid was washed with water and dried under vacuum with CaH_2. Yield: 434 mg (87 %) of $Mo_2O_4(OH)_4(GlyH)$.

Reaction **IV** - Compound $Na_2MoO_4 \cdot 2H_2O$ (779 mg, 3.22 mmol) and glycine (121 mg, 1.61 mmol) were dissolved in 17 mL of water and stirred at room temperature. Initial concentrations, for a 17 mL total volume, were $1.89 \cdot 10^{-1}$ M for molybdenum and $9.47 \cdot 10^{-2}$ M for glycine. The colourless pH = 7.39 solution was titrated with solution *B*. After the addition of 5.00 mL (5.42 mmol of HNO_3), the reaction mixture became opalescent and then a colourless solid was formed. After the addition of 7.00 mL (7.59 mmol of HNO_3), the reaction mixture was filtered (final pH = 1.04). The solid was washed with water, then dried under vacuum with CaH_2. Yield: 564 mg (88 %) of $Mo_2O_4(OH)_4(GlyH)$.

Reaction **V-1** - Compound $Mo_2O_4(OH)_4(GlyH)$ (434 mg, 1.09 mmol) was suspended in 20 ml of water and stirred at room temperature. The reaction mixture was titrated with solution *A*. The colourless solid was completely dissolved only after the addition of 8.10 mL (1.57 mmol of NaOH). After the addition of 11.1 mL (2.15 mmol of NaOH), 2 mL of the reaction mixture were taken (final pH = 5.31). The solvent was completely removed under vacuum from this aliquot of solution and a crystalline colourless solid was obtained. IR (ATR): $\tilde{v}/cm^{-1}$ = 3300-3000 (s, br); 1611 (s); 1485 (s); 1442 (m); 1407 (s); 1330 (s); 1117 (w); 1037 (w); 873 (s); 831 (s); 667 (w)

This product is a mixture of an inorganic molybdate and glycine. When the test tube containing the solid was heated with a Bunsen burner, MoO_3 sublimed and recondensed on the walls, while the

residue darkened.

Reaction **V-2** - The colourless solution, obtained after alkaline dissolution of $Mo_2O_4(OH)_4(GlyH)$, was stirred at room temperature and retro-titrated with solution *B*. After the addition of 2.05 mL (2.22 mmol of HNO_3), the reaction mixture became opalescent and then a colourless solid was formed. After 960 minutes, the reaction mixture was filtered (final pH = 2.18). The solid was washed with water, then dried under vacuum with CaH_2. Yield: 411 mg (95 % respect to initial amount) of $Mo_2O_4(OH)_4(GlyH)$.

Reaction **VI** - Compound $Na_2MoO_4 \cdot 2H_2O$ (976 mg, 4.04 mmol) was dissolved in 20.0 mL of water. The resulting pH = 8.57 solution was stirred at room temperature and titrated with solution *B*. After the addition of 6.10 mL (6.61 mmol of HNO_3), pH = 1.87 was obtained. At this point, glycine (151 mg, 2.01 mmol) was added. Initial concentrations, for a 26.1 mL total volume, were $1.55 \cdot 10^{-1}$ M for molybdenum and $7.74 \cdot 10^{-2}$ M for glycine. After ca. 2 minutes, the solid glycine was completely dissolved and the pH stabilized at 2.72. After 19 minutes the reaction mixture became opalescent and after 33 minutes a colourless solid was formed. After 277 minutes, the reaction mixture was filtered (final pH = 4.17). The solid was washed with water, then dried under vacuum with CaH_2. Yield: 333 mg (41 %) of $Mo_2O_4(OH)_4(GlyH)$.

Section 2.10 - Solubility and reactivity of $Mo_2O_4(OH)_4(aaH)$ in various solvents

H₂O, room temperature - Complexes **1-4** and **6** (about 20 mg) were stirred at room temperature in 0.5-1.0 mL of D_2O for a given time. The solid was not dissolved completely and no colour change in solution occurred but the pH decreased to about 3. The ^1H NMR spectrum of the solution showed only very weak signals which are consistent for the amino acid in solution. Only for **1** and **6**: the colourless undissolved solid was collected by filtration and dried in the oven at 60 °C. This product was identified as $Mo_2O_4(OH)_4(aaH)$ from its ATR spectrum (not reported) and it was recovered in almost quantitative yield. Details for each complex are given in table 1.

Tab. 1. ^{1}H NMR spectra and pH of the solutions obtained by stirring complexes **1-4** and **6** in water

Complex	Stirring time and solution pH	^{1}H NMR (D$_2$O): δ/ppm (very weak signals)
Mo$_2$O$_4$(OH)$_4$(GlyH)	2 hours pH = 3.2	3.50 (CH$_2$)
Mo$_2$O$_4$(OH)$_4$(PheH)	20 hours pH = 2.4	7.35-7.22 (5.0H, Ph); 4.03 (multiplet ABX pattern, 0.9H, CH); 3.22 (multiplet ABX pattern, 1.0H, CHH'); 3.00 (multiplet ABX pattern, 0.9H, CHH') - identical spectrum after 4 days
Mo$_2$O$_4$(OH)$_4$(LeuH)	3 hours	3.83 (multiplet ABX pattern, 1.0H, CHN); 1.73-1.60 (3.1H, CHMe$_2$ and CH$_2$); 0.86 (pseudo-t, ^{3}J$_{H-H}$ = 5.3 Hz, 6.1H, CH$_3$)
Mo$_2$O$_4$(OH)$_4$(MetH)	3 hours	3.84 (multiplet ABX pattern, 1.0H, CH); 2.55 (t, ^{3}J$_{H-H}$ = 7.4 Hz, 2.0H, SCH$_2$); 2.15-2.00 (2.2H, CHH'CH and CHH'CH); 2.03 (s, 2.8H, SCH$_3$)
Mo$_2$O$_4$(OH)$_4$((NMe$_2$)PheH)	20 minutes pH = 3.4	7.27–7.38 (5.0H, Ph); 3.85-3.81 (1.1H, CH); 3.34-3.28 (1.1H, CHH'); 3.13-3.06 (1.1H, CHH'); 2.95-2.85 (6.0H, NCH$_3$)

Note: no multiplet detail is given for a superimposition of multiplets (e.g. Ph hydrogens). Signals for complex 6 were too weak to discern the type of multiplet

MeOH, EtOH, ^{i}PrOH, room temperature - Compound **5** (60 mg, 0.14 mmol) was stirred in 1 mL of MeOH at room temperature for 24 hours. The solid was not dissolved completely and no colour change in solution occurred. The UV-Vis spectrum of the solution was recorded. The colourless solid was then collected by filtration and its IR spectrum was recorded. This procedure was repeated with EtOH and ^{i}PrOH. For each solvent, the undissolved solid was identified as Mo$_2$O$_4$(OH)$_4$(ProH) from its IR spectrum (not reported). UV-Vis (MeOH solution): λ/nm = 225 (strong absorption). UV-Vis (EtOH and ^{i}PrOH solutions): no absorptions (200-1100 nm).

MeOH, refluxing conditions - A suspension of **2** (101 mg, 0.21 mmol) in 30 mL of MeOH was stirred and heated until refluxing. The solid was completely dissolved in 1 hour. The resulting colourless solution was allowed to evaporate slowly at room temperature. A pale light-blue colour appeared after 24 hours, which intensity increased in the following days. After 13 days, a pale light blue solution (2-3 mL) and a light blue solid were obtained. This solution showed a strong UV absorption at 236 nm. GC-MS qualitative analysis revealed a major presence of L-phenylalanine, methyl ester. Smaller peaks were attributed to methyl formate and benzonitrile. The light-blue solid was collected by filtration, washed with acetone, diethyl ether and dried under vacuum with P$_4$O$_{10}$.

IR (ATR): $\tilde{\upsilon}$/cm^{-1} = 3482 (w, br); 3024 (mw, br); 2955 (mw, br); 1738 (m); 1595 (m, br); 1495 (s); 1457 (m); 1439 (m); 1386 (w); 1284 (m); 1240 (m); 1136 (w); 1080 (w); 941 (s); 898 (s); 866 (sh); 843 (s); 795 (mw); 744(w); 698 (m); 658 (w).

The solid was stirred with 1 ml of D$_2$O. NMR spectra of the resulting solution showed L-phenylalanine and its methyl ester in a 1 : 1.3 molar ratio. NMR signals attributed to the latter are italicized. ^{1}H NMR (D$_2$O): δ/ppm = 7.38-7.23 (Ph and *Ph*); 4.39 (multiplet ABX pattern, *CH*); 4.10 (multiplet ABX pattern, CH); 3.78 (s, *OMe*); 3.30 and 3.19 (multiplet ABX patterns, *CH$_2$*);

3.27 and 3.11 (2 multiplet ABX pattern, CH_2). $^{13}C\{^1H\}$ NMR (D_2O): δ/ppm = 134.6 (*Ph*) ; 133.7 (Ph); 129.4 (Ph / *Ph*); 129.3 (Ph / *Ph*); 128.1 (Ph / *Ph*) ; 127.8 (Ph / *Ph*); 55.2 (CH) 54.1 (*CH*) ; 53.6 (*OMe*); 36.0 (CH_2); 35.6 (*CH_2*).

MeOH/H₂O = 1 : 2, refluxing conditions - A suspension of compound **2** (98 mg, 0.20 mmol) in 20 mL of water was stirred at room temperature and 3 M HNO_3 was added to lower the pH from 2.4 to 2.0. Then 10 mL of MeOH were added and the mixture was stirred and heated until refluxing. After 6 hours, the solid was completely dissolved. The resulting pale yellow solution was allowed to evaporate slowly at room temperature. A pale light-blue colour appeared after 17 hours. GC-MS qualitative analysis of the solution revealed the presence of CO_2 and benzonitrile in a small amount. After 13 days, ca. 10 mL of a pale light-blue solution and a microcrystalline colourless solid were obtained. The solid was collected by filtration, washed with acetone, diethyl ether and identified as $Mo_2O_4(OH)_4(PheH)$ from its IR spectrum (not reported).

MeCN, room temperature - A suspension of **1** (333 mg, 0.83 mmol) in 10 mL of MeCN was stirred at room temperature. No visible changes occurred in both solid and liquid phases in the next 24 hours. The undissolved solid was collected by filtration and dried under vacuum with CaH_2. Yield: 288 mg (86 % respect to the initial amount) of $Mo_2O_4(OH)_4(GlyH)$. IR (ATR): $\tilde{\upsilon}/cm^{-1}$ = 2968 (w); 1626 (w); 1590 (w); 1521 (w);1484 (w);1456 (w); 1437(m); 1413 (m); 1372 (m); 1344 (m); 1300 (m); 1259 (s); 1185 (w); 1154(w); 1091 (m); 1023 (s); 950 (s); 921 (s); 905 (s); 792 (s); 721 (m); 689 (m).

DMSO - Complexes **1-6** (100-200 mg) were stirred at room temperature in 2-3 mL of DMSO. Yellow solutions were obtained following the immediate dissolution of **2**,**3**,**4** and **6**. Compound $Mo_2O_4(OH)_4(GlyH)$ was dissolved slowly at room temperature (> 24 hours) but rapidly when the suspension was heated at 100 °C (10 min) or 50 °C (30 min). A yellow solution was obtained also in this case. Compound $Mo_2O_4(OH)_4(ProH)$ was dissolved slowly at room temperature (> 3 days) and a green solution was initially obtained, which turned blue in the subsequent days. NMR spectra in DMSO-d_6 of the aforementioned solutions are reported below. The signals attributable to a second and / or a third amino acid molecule are italicized. Signals in ^1H spectra were always broadened thus no multiplet details are reported.

Tab. 2. ^1H and ^{13}C NMR spectra of the solutions obtained by dissolving $Mo_2O_4(OH)_4(aaH)$ in DMSO-d_6

Complex	^1H NMR: δ/ppm	$^{13}C\{^1H\}$ NMR: δ/ppm
$Mo_2O_4(OH)_4(GlyH)$	7.93 (2.8H); 4.45 (6.3H, $(CH_3)_2SO{-}Mo$); 3.61 (2.0H, CH_2); 3.27 ; 2.97	169.6 (CO); 45.6 (CH_2)
$Mo_2O_4(OH)_4(PheH)$	8.12 (1.4H); 7.28 (5.0H, Ph / Ph); 4.13 (8.0H*, CH); 3.98 (8.0H*,$(CH_3)_2SO{-}Mo$); 3.59 (8.0H*,CH); 3.08 (CH_2); 2.98; 2.93 (CH_2)	177.9 (CO); 177.4 (CO); 171.0 (CO); 138.0 (Ph); 135.4 (Ph); 129.9 (Ph / Ph); 129.0 (Ph); 128.9 (Ph); 127.7 (Ph); 127.0 (Ph); 58.0 (CH); 57.7 (CH); 53.8 (CH); 38.4 (CH_2); 36.3 (CH_2)
$Mo_2O_4(OH)_4(LeuH)$	8.09 (2.4H); 4.05 (5.9H, $(CH_3)_2SO{-}Mo$); 3.78 (0.8H, CH); 3.28 (CH); 1.69 (2.8H*, $CHMe_2$ / $CHMe_2$); 1.56 (2.8H*, CH_2 / CH_2); 0.87 (6.0H, CH_3 / CH_3)	171.9 (CO); 58.8 (CH); 51.1 (CH); 24.2 ($CHMe_2$); 23.6 ($CHMe_2$); 22.7 (CH_3); 22.2 (CH_3); 21.6 (CH_3)
$Mo_2O_4(OH)_4(MetH)$	8.08 (2.2H); 4.30 (7.0H*, $(CH_3)_2SO{-}Mo$); 3.88 (7.0H*, CH); 3.38 (7.0H*, CH); 2.94; 2.01 (5.8H§, SCH_3); 1.76 (5.8H§, SCH_3).	178.8 (CO); 178.0 (CO); 171.3 (CO); 55.7 (CH); 55.5 (CH); 51.7 (CH); 32.1 ($CHCH_2$); 31.1 ($CHCH_2$); 30.2 (SCH_2); 30.0 (SCH_2); 29.0 (SCH_2); 14.7 (SCH_3 / SCH_3)
$Mo_2O_4(OH)_4(ProH)$	9.22; 4.23 (7.0H*, CH); 3.93 (7.0H*, $(CH_3)_2SO{-}Mo$); 3.23 (1.7H, CH_2N); 2.05 ($C\underline{H}_2CH$); 1.84 ($C\underline{H}_2(CH_2)_2$); 1.71 ($C\underline{H}_2(CH_2)_2$)	179.4 (CO); 179.5 (CO); 171.6 (CO); 63.0 (CH); 62.6 (CH); 60.1 (CH); 46.2 (CH_2N); 30.1 ($\underline{C}H_2CH$); 28.6 ($\underline{C}H_2CH$); 25.9 ($\underline{C}H_2(CH_2)_2$); 23.7 ($\underline{C}H_2(CH_2)_2$)
$Mo_2O_4(OH)_4((NMe_2)PheH)$	7.29; 4.14 (CH); 3.66 ($(CH_3)_2SO{-}Mo$); 3.28-3.00 (CH_2); 2.78 (NCH_3); 2.70 (NCH_3); 2.69 (NCH_3)	175.5 (CO); 169.8 (CO); 140.7 (Ph); 136.1 (Ph); 129.6 (Ph / Ph); 128.9 (Ph / Ph); 127.4 (Ph); 126.4 (Ph); 72.7 (CH); 68.3 (CH); 33.3 (CH_2); 29.8 (CH_2)

*,§ Partially overlapping signals

Section 2.11 - Catalytic oxidations of cyclohexene

General procedure for catalytic reactions

Cyclohexene (400 μL, 3.95 mmol), 35 % H_2O_2 (1.2 mL, 14 mmol) and acetonitrile (6.0 mL) were added to a schlenk tube equipped with a water condenser, to avoid a major loss of Cy during the reaction. The H_2O_2/Cy molar ratio of the resulting solution was 3.5 and cyclohexene concentration was approximately 0.5 M. A given amount of $Mo_2O_4(OH)_4(aaH)$ (unless otherwise specified) was added and the resulting suspension was stirred and heated on a silicone oil bath at 65 ±2 °C. The solid was completely dissolved in the reaction medium after some time, developing a yellow colour in solution. The reaction was allowed to proceed for a selected interval of time. Successively, the schlenk tube was stored at 4 °C. The reaction mixture did not change at this temperature (checked by comparison of NMR spectra). The analysis of the reaction mixture was performed by means of NMR spectroscopy. Organic compounds were identified by comparison with the *AIST* spectral database[186] and quantified by using chlorobenzene (PhCl) as internal standard. This procedure was adopted for all the reactions reported below.

NMR analysis - At the end of the reaction, PhCl (100 µL, 0.986 mmol) was added to the reaction mixture, then ca. 0.2 mL of the solution was transferred into a NMR tube filled with 0.2-0.3 mL of CDCl$_3$. Alternatively, for reaction monitoring, PhCl was added at the beginning of the reaction and samplings of the solution were made at selected time intervals. The NMR tube was kept at 4 °C until spectra acquisition. The formation of two immiscible liquid phases in the NMR tube was observed. It is reasonable to assume that the yellow upper phase was made up of water (with some acetonitrile dissolved in it), while the colourless and more dense one was a mixture of CDCl$_3$ and acetonitrile. The distribution of organic compounds between the two phases and the not good magnetic field shimming, due to phase inhomogeneity, contributed to the broadening of ^{1}H resonances. For this reason, only chemical shift values are reported for ^{1}H spectra.

^{1}H and ^{13}C NMR chemical shifts of compounds identified in the reaction mixture are reported in table 3, while the unassigned ones are listed for each reaction.[h] The signals of the CH hydrogens (marked with *1* in table 3) were used for quantification.

Tab. 3. Chemical shifts (in ppm) with relative assignment for cyclohexene, cyclohexene oxide, *trans*-1,2-cyclohexanediol and *cis*-1,2-cyclohexanediol found in NMR spectra of catalytic reactions

Cyclohexene		Cyclohexene oxide		*trans*-1,2-Cyclohexanediol		*cis*-1,2-Cyclohexanediol	
^{1}H NMR	^{13}C NMR	^{1}H NMR	^{13}C NMR	^{1}H NMR	^{13}C NMR	^{1}H NMR	^{13}C NMR
1 : 5.37	*1* : 126.8	*1* : 2.82	*1* : 54.9	*1* : 3.02	*1* : 74.9	*1* : 3.24	*1* : 71.5
3 : 1.32	*2* : 24.6		*2* : 24.8	*3,3'* : 0.99	*2* : 32.4	*3,3'* : 1.40	*2* : 28.0
	3 : 22.1		*3* : 18.0		*3* : 23.9		*3* : 23.6

Monitoring of reactions with variable amounts of Mo$_2$O$_4$(OH)$_4$(GlyH)

Reaction with R = 67 - Compound Mo$_2$O$_4$(OH)$_4$(GlyH) (12 mg, 30 µmol) was used, resulting in a cyclohexene/molybdenum molar ratio of 67. The solid was dissolved almost immediately and a pale yellow solution resulted. The reaction mixture maintained this appearance for the subsequent 23 hours. The NMR characterization of the reaction mixture is reported in table 4.

Reaction with R = 32 - Compound Mo$_2$O$_4$(OH)$_4$(GlyH) (25 mg, 62 µmol) was used, resulting in a cyclohexene/molybdenum molar ratio of 32. The solid was dissolved within 85 minutes and a pale yellow solution resulted. This colour remained for 8 hours then changed to dark green (24

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h Due to broad resonances of acetonitrile (1.68 ppm with satellite signals at 1.90 and 1.55 ppm),[184] water (found at 4.47 ppm in the initial reaction mixture, then shifted to 4.0 ppm and finally to 3.2 ppm)[184] and hydrogen peroxide (found at 5.26 ppm in the initial reaction mixture, then shifted to 4.5 ppm),[185] many ^{1}H signals are hidden (e.g. the ones missing in table 3)

hours) and finally to dark brown (4 days). The NMR characterization of the reaction mixture is reported in table 5.

Reaction with R = 16 - Compound $Mo_2O_4(OH)_4(GlyH)$ (50 mg , 124 μmol) was used, resulting in a cyclohexene/molybdenum molar ratio of 16. The solid was not dissolved completely and an opalescence remained in the yellow solution until the end of the reaction (7.5 hours). The NMR characterization of the reaction mixture is reported in table 6.

Tab. 4. NMR yields, conversion and unassigned signals (in ppm) for reaction with $R = 67$

Reaction time, hours	1.34	4.47	7.26	11.73	30.37
Cy, *% Conversion*	18	42	56	67	92
trans-Cy(OH)₂, *% Yield*	4.6	15	20	23	23
cis-Cy(OH)₂, *% Yield*	0	3	6	7	2
CyO, *% Yield*		< 1	< 1	< 1	< 1
Unassigned — *¹³C NMR, ppm*	87.6 26.0 23.3	124.3	26.0	124.4 87.7 72.3 30.8; 26.1	124.3 87.6 26.1
Unassigned — *¹H NMR, ppm*	5.46	5.70 4.10 3.36	5.70 5.09 4.11 3.36	5.75 5.21 5.16 5.09 4.18 3.40 1.41	6.44 5.75 4.11 3.42

Tab. 5. NMR yields, conversion and unassigned signals (in ppm) for reaction with $R = 32$

		0.89	1.90	3.13	4.36	5.70	7.48	9.38	10.72
Reaction time, hours		0.89	1.90	3.13	4.36	5.70	7.48	9.38	10.72
Cy, *% Conversion*		20	33	56	71	84	94	98	99
trans-Cy(OH)₂, *% Yield*		8	22	36	39	41	43	42	40
cis-Cy(OH)₂, *% Yield*		1	4	4	6	4	4	1	1
CyO, *% Yield*			< 1	< 1	< 1	< 1	< 1	< 1	
Oxamide (CONH₂)₂	*¹³C NMR, ppm*								
	¹H NMR, ppm						7.81	7.85	7.82
Unassigned	*¹³C NMR, ppm*		124.3 87.6 26.0 23.3	87.6 26.0 23.3	153.8 124.3 100.8 87.5 26.0	124.3 100.8 87.6 33.3 30.8 26.0 23.3	124.3 100.8 87.5 33.2 25.9 23.3	124.4 100.8 87.6 73.3 33.1 30.8 29.9 26.1 24.7 23.4	133.5 124.4 100.7 87.6 73.2 33.7 33.3 33.1 26.0 23.3 30.8
	¹H NMR, ppm	5.66 5.55 4.09 3.37	5.66 5.43 4.08 3.35	5.69 5.43 4.09 3.36 1.75 1.40	5.65 4.07 3.34 3.16 1.06	6.88 5.69 5.44 5.17 4.09 3.36 1.80	6.75 5.64 5.39 4.04 3.34 1.07	6.82 6.57 5.72 5.42 4.87 4.80 4.70 4.13 1.38	6.80 6.53 5.68 5.44 4.73 4.10 3.63 3.35 1.38 1.13

Tab. 6. NMR yields, conversion and unassigned signals (in ppm) for reaction with $R = 16$

		0.67	1.54	2.81	3.55	4.56	7.35
Reaction time, hours		0.67	1.54	2.81	3.55	4.56	7.35
Cy, *% Conversion*		40	56	75	83	92	98
trans-Cy(OH)₂, *% Yield*		12	22	33	41	40	35
cis-Cy(OH)₂, *% Yield*		1	5	5	8	3	1
CyO, *% Yield*		< 1	< 1	< 1		< 1	
Oxamide (CONH₂)₂	*¹H NMR, ppm*					7.83	7.83
	¹³C NMR, ppm		124.4	133.6 124.3 100.9	124.4 33.6 29.9	124.4 30.1	124.0 30.4
Unassigned	*¹H NMR, ppm*	5.69 4.13 3.40	5.71 4.14 3.42 3.33	5.69 5.44 4.13 4.06	5.69 4.93 4.66 4.08	5.69 5.44 4.72 4.11 3.37 1.12	5.69 5.42 4.95 4.72 4.08 3.08 2.97 1.37

Two-component reactions in the same experimental conditions

Three reactions were carried out under the typical experimental conditions but each one without a different component (molybdenum complex, substrate or oxidant). A fourth reaction was carried out to investigate the catalytic activity of $Na_2MoO_4 \cdot 2H_2O$ under these conditions. Reactions were allowed to proceed for 112 hours.

Reaction without molybdenum complex (#1) - A sample of the colourless reaction mixture was taken after 3 hours. The solution became pale yellow after 40 hours and then maintained this appearance. The organic products identified at the end of the reaction were *trans*-1,2-cyclohexanediol and acetamide.

^{1}H NMR (CDCl$_3$, 3 h): δ/ppm = 5.67; 5.45 (C*H*=C*H*); 2.93 (C*H*OH); 1.40 (C*H$_2$*CH$_2$CH=CH); 1.05 (C*H$_2$*CH$_2$CHOH). Cy conversion = 1 % ; *trans*-Cy(OH)$_2$ yield = 1 %.

^{13}C{^{1}H} NMR (CDCl$_3$, 3 h): δ/ppm = 126.9 (CH=CH); 24.8 (*C*H$_2$CH=CH); 22.3 (*C*H$_2$–CH$_2$CH=CH).

^{1}H NMR (CDCl$_3$, 112 h): δ/ppm = 9.18 (br); 6.84; 6.47; 6.14; 5.85; 2.97 (C*H*OH); 2.81; 0.91 (C*H$_2$*CH$_2$CHOH). Cy conversion = 100 % ; *trans*-Cy(OH)$_2$ yield = 30 %.

^{13}C{^{1}H} NMR (CDCl$_3$, 112 h): δ/ppm = 191.2; 176.1; 74.8 (*C*HOH); 32.7 (*C*H$_2$CHOH); 23.8 (*C*H$_2$CH$_2$CHOH); 21.1 (*C*H$_3$CONH$_2$).

Reaction without substrate (#2) - Compound $Mo_2O_4(OH)_4$(GlyH) (25 mg, 62 μmol) was used. This solid was dissolved in about 30 minutes and a yellow solution was obtained. The reaction mixture maintained this appearance for 40 hours. An olive green solution and a colourless solid resulted after 112 hours. The only organic product identified was oxamide (($CONH_2$)$_2$).

^{1}H NMR (CDCl$_3$): δ/ppm = 7.82 (CONH$_2$); 6.87; 6.55; 5.85; 4.41; 4.00; 3.85.

^{13}C{^{1}H} NMR (CDCl$_3$): δ/ppm = 162.3 (CONH$_2$).

Reaction without oxidant (#3) - Compound $Mo_2O_4(OH)_4$(GlyH) (25 mg, 62 μmol) was used, resulting in a cyclohexene/molybdenum molar ratio of 32. The solid remained mostly undissolved up to 40 hours but a colourless solution resulted after 112 hours. No other organic product except cyclohexene was identified.

^{1}H NMR (CDCl$_3$): δ/ppm = 5.40 (2H, C*H*=C*H*); 5.33; 2.00 (C*H$_2$*CH=CH); 1.35 (4H, C*H$_2$*CH$_2$CH=CH).

^{13}C{^{1}H} NMR (CDCl$_3$): δ/ppm = 126.1 (CH=CH); 24.6 (*C*H$_2$CH=CH); 22.1 (*C*H$_2$–CH$_2$CH=CH).

A whitish solid resulted after the solvent was completely removed by heating (40 °C) under

vacuum. This product showed some additional IR bands compared to $Mo_2O_4(OH)_4(GlyH)$. IR (ATR): $\tilde{\upsilon}/cm^{-1}$ = 3554 (w, br); 3383 (w, br); 2965 (m); 2922 (m); 2872 (w, br); 1716 (w); 1606 (m); 1583 (m); 1505 (m); 1451 (m); 1408 (s); 1340 (m); 1309 (w); 1286 (w); 1260 (m); 1230 (w); 1205 (w); 1106 (w); 1038 (w); 946 (s); 916 (s); 890 (s); 803 (w); 767 (m).

Reaction with Na₂MoO₄ (#4) - Compound $Na_2MoO_4 \cdot 2H_2O$ (15 mg, 62 μmol) was used, resulting in a cyclohexene/molybdenum molar ratio of 32. Sodium molybdate immediately turned into a dark red oil in the bottom of the reaction mixture. During the next 15 minutes, this product was slowly dissolved in the solution and the formation of a gaseous product was observed. The resulting orange solution became colourless after 40 hours and pale yellow-orange after 112 hours. The only oxidation product of cyclohexene was 2-cyclohexenone.

^{1}H NMR (CDCl₃): δ/ppm = 5.51; 5.45; 5.41 (CH=CH); 6.80 (1H, C*H*=CHCO); 5.71 (1H, CH=C*H*CO); 2.84; 2.14 (4H, C*H₂*CO and C*H₂*CH=CH). Cy(–2H)O yield = 27 %.

^{13}C{^{1}H} NMR (CDCl₃): δ/ppm = 199.5 (CO); 151.2 (*C*H=CHCO); 129.1 (*C*HCO); 37.6 (*C*H₂CO); 25.2 (*C*H₂CH=CH); 22.4 (*C*H₂(CH₂)₂); 21.4 (*C*H₃CONH₂).

A brown oil and sublimed colourless crystals resulted when the solvent was completely removed under vacuum at 40 °C. This product was identified as acetamide. IR (ATR): $\tilde{\upsilon}/cm^{-1}$ = 3346 (m); 3290 (sh); 3154 (m); 3002 (w); 2959 (w); 2823 (w); 1749 (w); 1643 (s); 1467 (m); 1445 (m); 1392 (s); 1354 (m); 1260 (m); 1152 (m); 1092 (m); 1047 (m); 1010 (m); 876 (w); 798 (m); 678 (w)

^{1}H NMR (D₂O): δ/ppm = 1.88 (CH₃). ^{13}C NMR (D₂O): δ/ppm = 177.3 (CO); 21.2 (CH₃).

Procedure for separation and analysis of organic products and molybdenum derivative

After the NMR analysis, the reaction mixture was transferred in a 10 mL round-bottom flask. Acetonitrile, non-reacted cyclohexene and other volatile compounds were removed under vacuum at 40 °C with intense stirring for about 10 minutes. Caution is needed during this operation because a high temperature (80 °C) caused an explosion in the distillation residue. About 50 mg of NaCl were added to the wet solid distillation residue, then organic compounds were extracted with 3 x 3 mL of diethyl ether. Organic products were quantified with GC-FID. When the catalytic activity of chiral complexes **2-6** was investigated, the enantiomeric excess of *trans*-Cy(OH)₂ was measured by polarimetry. The solid residue remaining after extraction was dried under vacuum and its IR spectrum was recorded. This procedure is shown in figure 33.
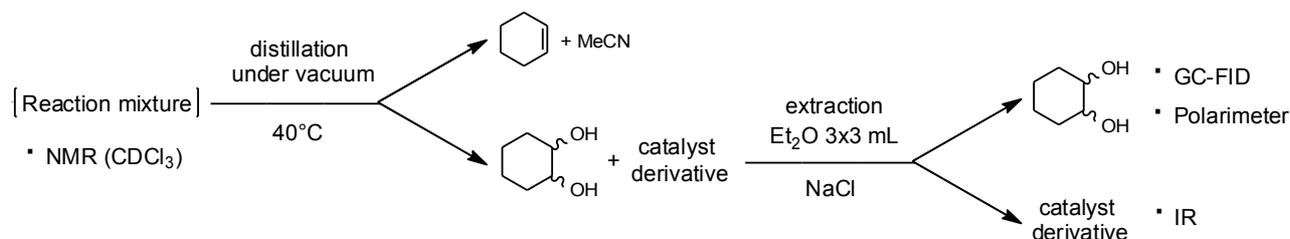
Fig. 33. Scheme of the separation procedure described

The effectiveness of this separation procedure was verified in the following ways.

1) A catalytic reaction with $Mo_2O_4(OH)_4(GlyH)$ was carried out under the usual conditions (reaction *1* in the next paragraph) and the final reaction mixture was subjected to this procedure.

The colourless distillate solution was collected in a schlenk cooled with liquid nitrogen. A sample of this solution was transferred in an NMR tube filled with 0.3 mL $CDCl_3$ and NMR spectra revealed the sole presence of cyclohexene and acetonitrile.

The colourless diethyl ether solution was subjected to NMR analysis (with $CDCl_3$) and revealed the presence of *trans*-1,2-cyclohexanediol, *cis*-1,2-cyclohexanediol, cyclohexene oxide and other unidentified products. After the GC-FID analysis, diethyl ether was removed and a viscous pale yellow liquid resulted. The IR spectrum clearly identified *trans*-1,2-cyclohexanediol[186] and showed no strong bands in the range 1000-800 cm^{-1}.[i] IR (ATR): $\tilde{v}/cm^{-1}$ = 3330 (s, br); 2935 (s); 2861 (s); 1630 (m); 1559 (m); 1451 (s); 1406 (s); 1375 (s); 1346 (s); 1307 (m); 1275 (m); 1234 (m); 1195 (w); 1164 (w); 1118 (m); 1066 (s); 1041 (s); 951 (w); 927 (m); 855 (m); 784 (w); 722 (w); 697 (w); 636 (m); 610 (m); 574 (m); 536 (m); 468 (w).

The yellow solid extraction residue was stirred with 1 mL of D_2O and a yellow solution resulted. After 48 hours, a pale yellow solution and a yellow solid were obtained. The IR spectrum of this solid, collected by filtration, showed strong bands in the 980-870 cm^{-1} region which are indicative of an oxoperoxo molybdenum complex.[53] IR (ATR): $\tilde{v}/cm^{-1}$ = 3400 (s, br); 3241 (sh); 2943 (m); 1739 (m); 1623 (s); 1593 (s); 1552 (m); 1521 (m); 1455 (m); 1419 (s); 1366 (w); 1341 (m); 1235 (m); 1099 (w); 1051 (w); 972 (m); 951 (s); 921 (s); 904 (s); 801(w); 760 (w); 705 (w); 667 (w).

^1H NMR spectrum of the D_2O solution showed no signal. This indicates that the extraction of the diols was quantitative. Since 1,2-cyclohexanediols are well soluble both in aqueous and organic solvents (log P_{OW} = 0.79 for *trans*-1,2-cylohexanediol[187] and 0.23 for *cis*-1,2-cyclohexanediol[188]), the presence of NaCl was necessary for a quantitative extraction. When no NaCl was added, *trans*- and *cis*-1,2-cyclohexanediol were found both in the diethyl ether solution and in the extraction residue (once dissolved in water).

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i   This wavenumber interval is typical for Mo–O stretching bands (see section 3.4)

2) Acetonitrile solutions with different concentrations of *trans*-Cy(OH)$_2$ were subjected to the procedure described (distillation + extraction) and an average recovery of 92 % (by GC-FID) for *trans*-Cy(OH)$_2$ was found.

GC-FID analysis - Decane (100 μL, 0.513 mmol) was added to the diethyl ether solution and used as internal standard. Chromatographic analyses were performed in triplicate. The response factor[189] of *trans*-Cy(OH)$_2$ versus decane using the flame ionization detector was determined to be 2.30 (the theoretical carbon atoms ratio is 1.67). This value was used also for calculating the yield of the *cis*- diastereomer.

Polarimetric analysis - Diethyl ether was removed by evaporation and the resulting residue was dissolved with a known amount of water (about 10 g). The optical rotation of this solution (α_{meas}) was measured and the enantiomeric excess (*ee*) of *trans*-Cy(OH)$_2$ was calculated with equation (12), where *l* is the pathlenght and $[\alpha]_\lambda^T$ is the optical rotatory power. A value of $[\alpha]_D^{20} = +39°$ for (1S,2S)-*trans*-1,2-cyclohexanediol in water has been reported.[190]

$$\alpha_{meas} = [\alpha]_\lambda^T \cdot l \cdot c \cdot ee \tag{12}$$

Catalytic activity of complexes 1-6 under the selected experimental conditions

Complexes **1-6** (124 μmol) were used, resulting in a cyclohexene/molybdenum molar ratio of 16. A yellow solution was obtained in each case. The reactions were allowed to proceed for 3 hours. The reactions (*1-6*) are named after the Mo$_2$O$_4$(OH)$_4$(aaH) complex used. The NMR characterization of the reaction mixtures is reported in table 7.

Tab. 7. NMR yields, conversion and unassigned signals (in ppm) for reactions 1-6

Reaction	1	2	3	4	5	6
aaH of Mo$_2$O$_4$(OH)$_4$(aaH)	GlyH	PheH	LeuH	MetH	ProH	(NMe$_2$)PheH
Cy, % Conversion	77	70	67	63	67	79
trans-Cy(OH)$_2$, % Yield	35	30	32	38	28	37
cis-Cy(OH)$_2$, % Yield	9	7	8	8	8	6
CyO, % Yield	< 1	< 1			< 1	< 1
^{13}C NMR, ppm — Unassigned	124.3 87.6 26.0	87.6 26.0 23.6 19.7	87.6; 26.1	87.6 26.5 23.6	124.3 87.6 30.1 26.0 23.5 20.0	124.4 26.1 23.6
^{1}H NMR, ppm	5.71 4.47 3.42	5.69 5.36 4.10 3.37	5.70 4.70 4.57 4.12 3.40	5.72 5.22 4.13 3.40 1.41	5.69 5.45 4.71 4.11 3.36 1.33 1.11	5.71 5.46 4.12 3.66 3.39 1.15

The reaction mixtures (*1-6*) were then subjected to the procedure of separation and analysis described above. Table 8 reports the results of chromatographic and polarimetric analysis.

Tab. 8. Chromatographic and polarimetric characterization of reactions *1-6*

t_R/min	3.04	3.23	3.50		3.99		6.20	
Compound*			*cis*-Cy(OH)$_2$		*trans*-Cy(OH)$_2$			Enantiomeric excess %
Reaction	Relative Area %	Relative Area %	Relative Area %	% Yield	Relative Area %	% Yield	Relative Area %	
1	1.9	2.5	24.4	7.7	100	31.7	7.0	-
2	1.1	1.8	17.1	5.7	100	33.4	3.0	5
3	1.2	1.9	22.7	6.4	100	26.8	2.1	1
4	0.8	1.1	17.0	5.0	100	31.6	3.6	5
5	1.5	2.1	21.3	4.8	100	23.1	3.3	3
6	1.4	1.2	13.5	4.3	100	31.6	2.9	5

* PhCl (t_R = 2.91 min) and decane (t_R = 3.73 min) have been omitted

Yellow solids were obtained as extraction residues for each reaction. IR spectra are reported in table 9. These compounds were partially (2,3) or completely (1,4-6) soluble in water, giving a yellow solution. Unfortunately, no signal was identified in ^{1}H NMR spectra (probably due to the small amount).

Tab. 9. IR spectra of residues for reactions 1-6

Reaction	IR (ATR): $\tilde{\upsilon}$/cm^{-1}
1	3423 (m); 3216 (m); 3194 (m); 2946 (m); 2896 (w); 1716 (w); 1660 (s); 1593 (m); 1487 (m); 1451 (w); 1431 (m); 1403 (m); 1378 (w); 1341 (w); 1292 (m); 1260 (m); 1105 (m); 1064 (m); 1041 (m); 969 (s); 899 (w); 877 (w); 857 (s)
2	3400 (s, br); 2938 (m); 2864 (m); 1638 (s); 1554 (m); 1454 (m); 1415 (w); 1270 (w); 1242 (w); 1097 (sh); 1069 (s); 1051 (s); 969 (s); 856 (s); 730 (w)
3	3300 (m, br); 3940 (s); 2863 (s); 1727 (w); 1653 (s); 1626 (m); 1551 (w); 1521 (w); 1450 (m); 1402 (m); 1375 (m); 1346 (m); 1306 (w); 1261 (m); 1235 (m); 1191 (w); 1113 (w); 1063 (s); 1040 (s); 968 (s); 926 (w); 855 (s); 792 (w)
4	3400 (m, br); 3200 (m, br); 3016 (m); 2931 (m); 2864 (m); 1735 (w); 1622 (s); 1513 (w); 1448 (m); 1417 (m); 1367 (w); 1289 (s); 1129 (s); 1065 (m); 1044 (m); 960 (s); 900 (s); 859 (s); 772 (w)
5	3300 (m, br); 2934 (m); 2860 (m); 1723 (m); 1615 (s); 1563 (m); 1446 (m); 1428 (m); 1372 (m); 1235 (m); 1182 (w); 1134 (w); 1064 (s); 1041 (s); 963 (s); 902 (s); 857 (m); 771 (w); 734 (w); 683 (w)
6	3360 (m, br); 2938 (m); 2861 (m); 1727 (w); 1628 (m); 1557 (w); 1497 (w); 1450 (m); 1403 (m); 1376 (m); 1350 (m); 1303 (w); 1261 (m); 1236 (m); 1193 (w); 1063 (s); 1040 (s); 967 (s); 926 (m); 857 (s); 801 (m); 751 (w); 701 (w)

Section 2.12 - Preparation of [aaH₂]NO₃ and [Na]aa

[GlyH₂]NO₃ - Glycine (335 mg, 4.46 mmol) was dissolved in 10 mL of 1.08 M HNO₃ (11 mmol). A colourless microcrystalline solid was formed in a period of 6 days by slow evaporation of the reaction mixture at room temperature. The solid was collected by filtration and dried under vacuum with CaH₂. ^{13}C NMR (CP-MAS solid state): δ/ppm = 171.7 (CO); 41.1 (CH₂). IR (ATR): ṽ/cm^{-1} = 3205 (m); 3150 (w); 3032 (m); 2966 (m); 2909 (m); 2837 (m); 2748 (w); 2719 (w); 2640 (m); 2541 (w); 2442 (w); 2332 (w); 2262 (w); 2236 (w); 2221 (w); 1986 (w); 1724 (s); 1627 (w); 1596 (w); 1517 (m); 1442 (m); 1416 (s); 1355 (s); 1331 (s); 1215 (s); 1124 (s); 1043 (s); 914 (s); 890 (s); 868 (s); 813 (s); 738 (m); 712 (w); 662 (w).

[PheH₂]NO₃ - L-Phenylalanine (488 mg, 2.95 mmol) was dissolved in 10 mL of water and 3.0 mL of 1.08 M HNO₃ (3.2 mmol) were added. The reaction mixture was allowed to evaporate slowly at room temperature and colourless crystals were formed in a period of 12 days. The solid was collected on filter paper and dried under vacuum with CaH₂. ^{13}C NMR (CP-MAS solid state): δ/ppm = 173.9 (CO); 173.2 (CO); 135.2 (Ph); ; 132.8 (Ph); 132.3 (Ph); 129.8 (Ph); 129.3 (Ph); 127.6 (Ph); 127.3 (Ph); 56.3 (CH); 55.5 (CH); 37.0 (CH₂); 36.3 (CH₂). IR (ATR): ṽ/cm^{-1} = 3148 (m, br); 3026 (m, br); 2972 (m, br); 1717 (s); 1667 (m); 1606 (w); 1584 (w); 1505 (m); 1496 (m); 1471 (w); 1453 (m); 1445 (m); 1408 (m); 1357 (s); 1335 (s); 1304 (m); 1200 (s); 1150 (m); 1119 (m); 1082 (w); 1045 (w); 1033 (w); 986 (w); 972 (w); 943 (w); 922 (w); 904 (w); 873 (w); 851 (w); 814 (m); 796 (w); 759 (w); 743 (sh); 737 (m); 693 (s).

[LeuH₂]NO₃ - L-Leucine (225 mg, 1.71 mmol) was dissolved in 10 mL of 1.08 M HNO₃ (10 mmol). Colourless needle-shaped crystals were formed in a period of 5 days by slow evaporation of the reaction mixture at room temperature. The solid was collected on filter paper and dried under vacuum with CaH₂. ^{13}C NMR (CP-MAS solid state): δ/ppm = 173.9 (CO); 173.1 (CO); 52.9 (CHN); 39.2 (CH₂); 24.7 (CHMe₂); 23.3 (CH₃); 22.3 (CH₃); 21.7 (CH₃); 20.0 (CH₃). IR (ATR): ṽ/cm^{-1} = 3221 (w); 3197 (w); 3149 (w); 2973 (m); 2958 (m); 2918 (m); 2875 (m); 2768 (w); 2701 (w); 2649 (w); 2583 (w); 2537 (w); 1717 (s); 1624 (m); 1579 (w); 1507 (s); 1473 (w); 1454 (m); 1413 (s); 1386 (s); 1344 (s); 1323 (s); 1297 (m); 1212 (s); 1171 (s); 1142 (s); 1075 (m); 1035 (s); 995 (m); 939 (m); 912 (s); 807 (s); 752 (w); 730 (w); 711 (m).

[MetH₂]NO₃ - L-Methionine (300 mg, 2.00 mmol) was dissolved in 2 mL of water and 2.0 mL of 1.08 M HNO₃ (2.2 mmol) were added. The reaction mixture was allowed to evaporate slowly at

room temperature. Pale yellow crystals were formed in a period of 21 days. The solid was collected on filter paper and dried under vacuum with CaH_2. ^{13}C NMR (CP-MAS solid state): δ/ppm = 173.7 (CO); 172.2 (CO); 54.6 (CH); 54.4 (CH); 32.9 (CH_2CH); 30.2 (SCH_2); 16.0 (SCH_3); 15.5 (SCH_3). IR (ATR): $\tilde{\upsilon}$/cm^{-1} = 3182 (m); 3044 (m); 2964 (m); 2921 (m); 2853 (m); 2713 (w); 2640 (w); 2604 (w); 1724 (s); 1620 (w); 1573 (w); 1506 (m); 1407 (s); 1381 (s); 1340 (s); 1287 (s); 1238 (m); 1225 (m); 1181 (s); 1135 (s); 1100 (m); 1073 (m); 1049 (m); 1035 (m); 984 (m); 948 (m); 913 (m); 864 (s); 817 (m); 773 (m); 756 (m); 731 (m); 700 (m); 655 (w).

Conversely this product was not obtained with excess acid: the solution slowly became intense yellow and a gaseous product was formed. This was probably due to an oxidation reaction of the amino acid caused by HNO_3.

L-Proline and *N,N*-dimethyl-L-phenylalanine salts with nitric acid were not obtained following this procedure. A viscous pale yellow liquid was obtained after several days from slowly evaporating aqueous solutions of these amino acids with a slight molar excess of nitric acid. No solidification occurred when the liquid was dried under vacuum with CaH_2, nor when it was kept at −30 °C for 20 days. An identical product was obtained when the liquid was dissolved in acetone and this solution was allowed to evaporate slowly at room temperature.

Na[Met] - L-Methionine (182 mg, 1.21 mmol) was dissolved in 4 mL of 1 M NaOH (4 mmol). The resulting solution was concentrated up to 1 mL under vacuum and then it was allowed to evaporate slowly at room temperature in a vacuum atmosphere. A colourless microcrystalline solid was formed after 24 hours. The solid was collected on filter paper and dried under vacuum with CaH_2. This compound is highly hygroscopic. ^{13}C NMR (CP-MAS solid state): δ/ppm = 183.9 (CO); 181.2 (CO); 56.6 (CH); 40.1 (CH_2CH); 37.3 (SCH_2); 33.6 (SCH_2); 31.8 (SCH_2); 16.9 (SCH_3); 16.5 (SCH_3). IR (ATR): $\tilde{\upsilon}$/cm^{-1} = 3436 (w); 3402 (w); 3360 (w); 3344 (w); 3307 (w); 3264 (m); 3039 (m); 2949 (m); 2914 (m); 2856 (m); 1705 (w, br);1563 (s);1483 (m); 1422 (s);1410 (s);1356 (s);1299 (w);1268 (w);1229 (w);1201 (w);1107 (w);1062 (w);1036 (w);956 (m); 916 (m); 879 (w); 844 (m); 770 (m); 718 (w); 659 (w).

Na[(NMe₂)Phe] - *N,N*-Dimethyl-L-phenylalanine (120 mg; 0.62 mmol) was dissolved in 3 mL of 1 M NaOH (3 mmol). The resulting solution was allowed to evaporate slowly at room temperature. After 5 days, the concentrated solution was cooled at 4 °C and a colourless microcrystalline solid was rapidly obtained. The solid was collected on filter paper and dried at 60 °C for 24 hours. The solid so obtained contained an Na_2CO_3 impurity (171.6 ppm on NMR spectrum[191]), probably due to the presence of traces of NaOH mother solution in the collected crystals. This compound is mildly

hygroscopic. ^{13}C NMR (CP-MAS solid state): 178.3 (CO); 176.9 (CO); 171.6 (Na$_2$CO$_3$); 144.4 (Ph); 143.8 (Ph); 142.2 (Ph); 133.8 (Ph); 132.7 (Ph); 130.6 (Ph); 128.3 (Ph); 126.0 (Ph); 124.8 (Ph); 73.7 (CH); 73.3 (CH); 72.9 (CH); 42.3 (NCH$_3$); 38.7 (NCH$_3$); 36.0 (NCH$_3$); 29.4 (CH$_2$). IR (ATR): $\tilde{\upsilon}$/cm^{-1} = 3187 (w); 3084 (w); 3062 (w); 3025 (w); 3004 (w); 2958 (w); 2924 (w); 2869 (w); 2833 (w); 2778 (w); 1603 (s); 1493 (s); 1454 (s); 1435 (m); 1393 (s); 1337 (w); 1323 (w); 1309 (w); 1285 (w); 1263 (w); 1225 (w); 1182 (w); 1162 (w); 1098 (w); 1076 (w); 1035 (m); 924 (w); 905 (w); 864 (m); 817 (w); 740 (m); 724 (m); 696 (s).

Following the procedure described for *N,N*-dimethyl-L-phenylalanine, the sodium salts of glycine, L-phenylalanine and L-proline were not obtained in a pure form, judging by their non-crystalline appearance and their solid state ^{13}C NMR spectra. For each amino acid, the NMR spectrum showed signals attributable to the amino acidate anion but also indicated the presence of another amino acid derivative. Moreover, a signal in the 163-168 ppm range suggested the presence of CO$_3^{2-}$ anion. Thus, the solid precipitated from the alkaline aqueous solution is probably a mixture of sodium amino acidate and another unidentified amino acid-sodium carbonate derivative. Since these solutions were allowed to evaporate slowly for 7-18 days, the long exposure to the air may have led to a partial carbonation of NaOH and thus to the formation of this second product.

CHAPTER 3

Results and discussion

Section 3.1 - Preparative hints of Mo$_2$O$_4$(OH)$_4$(aaH) complexes

Oxomolybdenum(VI) complexes **1-6** with general formula Mo$_2$O$_4$(OH)$_4$(aaH) were obtained, as colourless solids, from acidic aqueous solutions of a molybdate salt (Na$_2$MoO$_4$·2H$_2$O, (NH$_4$)$_2$MoO$_4$ or (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O) and an α-amino acid (glycine (**1**), L-phenylalanine (**2**), L-leucine (**3**), L-methionine (**4**), L-proline (**5**) and *N,N*-dimethyl-L-phenylalanine (**6**)).[j]

Compounds Mo$_2$O$_4$(OH)$_4$(aaH) were obtained under different experimental conditions. The formation of the same product was verified by comparison of solid state IR spectra and, in some cases, it was further confirmed by comparison of solid state NMR spectra and / or elemental analyses (C, H, N, Mo). Therefore, the influence of some experimental parameters on the formation of Mo$_2$O$_4$(OH)$_4$(aaH) complexes is described. These include the type of molybdate and acid used, the pH of the reaction mixture, initial metal-to-ligand molar ratio (M/L), initial molybdenum concentration ([Mo]$_0$) and temperature.

Aqueous solutions of amino acid and Na$_2$MoO$_4$ or (NH$_4$)$_6$Mo$_7$O$_{24}$ were acidified with HNO$_3$ up to pH = 2. Appropriate volumes of these solutions were mixed in order to obtain M/L = 2 : 1 and stirred at room temperature. Features of these reactions are summarized in table 10.

All of these reactions showed a similar trend: the solution turned opalescent after different periods of time depending on the amino acid and the formation of Mo$_2$O$_4$(OH)$_4$(aaH), as colourless or pale yellow solid, took place. An increase in pH after the formation of the solid was observed in each case. Yields of 82-92 % were obtained for GlyH, PheH, MetH and (NMe$_2$)PheH and of 73-77 % for ProH and LeuH.

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[j] As it will be explained in section 3.5, the proposed structure for these complexes is given by the formula [(MoO$_2$(OH))$_2$(μ-OH)$_2$(μ-O$_2$CCH(NH$_3$)R-κ*O*,κ*O'*)]. An oxo-bridged polymeric structure, obtained from the condensation of two terminal −OH ligands, is also probable. For the sake of simplicity, these complexes will be referred hereafter with the shortened formula Mo$_2$O$_4$(OH)$_4$(aaH).

Tab. 10. Reactions of Na_2MoO_4 / $(NH_4)_6Mo_7O_{24}$ with amino acids (RT, pH = 2 (HNO_3), M/L = 2 : 1, $[Mo]_0 \approx 0.1$)

Amino acid	Molybdate	Initial pH	Solid formation	Final pH (filtrate solution)	$Mo_2O_4(OH)_4(aaH)$ Yield
GlyH	Na_2MoO_4	1.8	after 25 min	3.2	90 %
	$(NH_4)_6Mo_7O_{24}$	1.6	after 5 min (opalescence)	2.1	92 %
PheH	Na_2MoO_4	1.9	after 2.5 h	2.5	90 %
	$(NH_4)_6Mo_7O_{24}$	1.6	after 4 h (opalescence)	2.1	86 %
LeuH	Na_2MoO_4	1.8	from the residue after complete evaporation	-	77 %
	$(NH_4)_6Mo_7O_{24}$	1.8	§	2.4	26 %
MetH	Na_2MoO_4	1.8	after 25 min	2.5	82 %
	$(NH_4)_6Mo_7O_{24}$	1.6	after 30 min (opalescence)	2.1	82 %
ProH	Na_2MoO_4	1.8	after 25 min	2.4	73 %
	$(NH_4)_6Mo_7O_{24}$	1.6	immediate	2.1	73 %
$(NMe_2)PheH$	Na_2MoO_4	2.0	immediate	2.4	83 %
	$(NH_4)_6Mo_7O_{24}$	1.6	immediate	2.1	90 %

§ This reaction is described separately

It may be noted that the same product was obtained from a given amino acid, regardless of the molybdate used. Moreover the reaction yield, the time interval before the formation of the solid and the pH change were little influenced by the molybdate precursor. These observations suggest that:

- The reactive oxomolybdenum species, stable at this pH value, is the same either when a monomeric molybdate ($[MoO_4]^{2-}$) or an isopolyanion ($[Mo_7O_{24}]^{6-}$) were used

- The compounds obtained are probably not ionic, since, for a specific amino acid, a product showing superimposable spectral features and similar elemental analyses was formed when changing the counterion (Na^+ or NH_4^+)

On the other hand, the reaction kinetics is very different depending on the amino acid used. For example, the reactions of both molybdates with $(NMe_2)PheH$ occurred instantaneously, while the formation of $Mo_2O_4(OH)_4(aaH)$ from Na_2MoO_4 and LeuH did not occur at all after 18 hours at room temperature and the product was recovered only from the residue after complete evaporation.

Under similar conditions, the formation of $Mo_2O_4(OH)_4(aaH)$ required a time interval that grows in the following order: $(NMe_2)PheH <$ ProH $\approx$ GlyH $<$ MetH $\ll$ PheH $\ll$ LeuH.

Reactions between Na_2MoO_4 and glycine were also performed in the same experimental conditions but with a different initial acid concentration: in one case 65 % HNO_3 was added until pH = 1 and in another case 1 M HNO_3 (pH ca. 0) was used as the solvent. A third reaction was carried out at pH = 1 with HCl, according to the procedure indicated by Furuhashi et al.[134] Table 11

reports a summary of these reactions, together with the reaction at pH = 2 for comparison.

Tab. 11. Reactions of Q_2MoO_4 (Q = Na, NH_4) with glycine in different acid concentrations (M/L = 2 : 1)

Reaction conditions	Na_2MoO_4, $[Mo]_0 \approx 0.1$ Room Temperature HNO$_3$			$(NH_4)_2MoO_4$, $[Mo]_0 \approx 0.04$ heated until boiling HCl
Initial pH	1.8	1.0	about 0	1
Product obtained	$Mo_2O_4(OH)_4(GlyH)$	$(MoO_3)_2(GlyH)\cdot 2H_2O$	$MoO_3\cdot nH_2O$	$Mo_2O_4(OH)_4(GlyH)$
Yield	90 %	86 %	< 26 %	100 %
Solid formation	after 25 min	after 5 h	did not form unless concentrating	after ca. 20 min

The complex $Mo_2O_4(OH)_4(GlyH)$ was obtained in quantitative yield from the reaction of $(NH_4)_2MoO_4$ with glycine at pH = 1 with HCl. Since the same product was obtained in the presence of different cations (Na^+, NH_4^+) and different anions (Cl^-, NO_3^-), it can be stated that these complexes are neutral, i.e. the complete formation reaction is (13). This can be hypothesized also for the other amino acids even if reactions were performed only with HNO_3.

$$2 \, Q_2MoO_4 + 4 \, HX + GlyH \longrightarrow Mo_2O_4(OH)_4(GlyH) + 4 \, AX \tag{13}$$

A different compound was obtained when the reaction was performed at pH = 1 at room temperature, the other experimental conditions being the same. This product shares common features with $Mo_2O_4(OH)_4(GlyH)$. Its non-ionic nature is postulated on the basis of analytical data and on the fact that it was formed in high yield (86 %) also from the reaction of $MoO_3\cdot H_2O$ with glycine under refluxing conditions. In addition, mainly $NaNO_3$ was identified from the filtered solution of the reaction mixture with M/L = 2 : 1. This suggests that also in this product the Mo/glycine ratio is 2 : 1. The molybdenum content (47.8 %) is compatible with the composition $(MoO_3)_2(GlyH)\cdot 2H_2O$.

The reaction mixture with $[H^+] \approx 1$ was stirred for 24 hours at room temperature, then heated for 4 hours at 70 °C and then kept for 24 hours at 4 °C but a solid was not obtained. A product was isolated from the colourless solution only after concentrating to a small volume ($[Mo] \approx 1$). This product is not **1**, but probably an hydrated form of MoO_3, judging by its IR spectrum.

In conclusion, $Mo_2O_4(OH)_4(GlyH)$ was obtained at pH = 2, a different 2 : 1 complex was obtained at pH = 1 and no amino acid complex was isolated in a more acidic environment (pH = 0), the other experimental conditions being the same (see figure 34). It is reasonable to suppose that these differences with pH changes are due to the various equilibria in which the Mo(VI) ion is involved (see section 1.1) and to the different reactivity of the predominant oxomolybdenum

species in solution towards ligands.
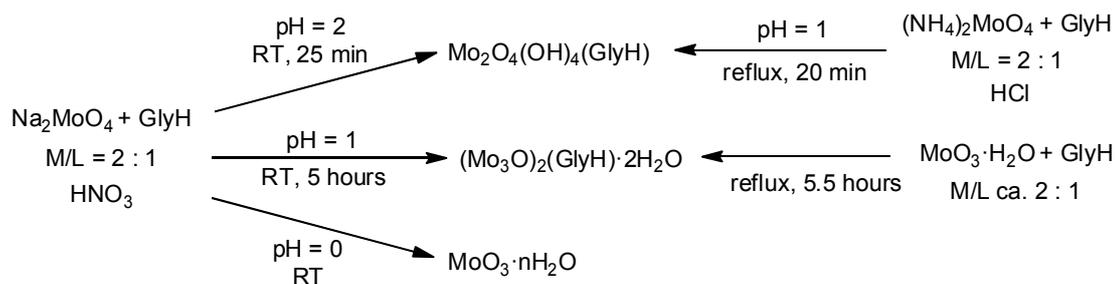
Fig. 34. Scheme of reactions performed at different acid concentrations and / or with various molybdenum(VI) sources

The formation of $Mo_2O_4(OH)_4(GlyH)$ in a pH = 1 solution was completely suppressed at room temperature, since a different complex was obtained in high yield. Hovever, **1** was formed quantitatively by refluxing the reaction mixture. This suggests that temperature exerts some effect on the chemoselectivity of reaction. In addition, the reaction in boiling HCl at pH = 1 was as fast as the one carried out at room temperature with HNO_3 at pH = 2, although the reaction mixture was ca. three times more diluted.

The effect of the M/L molar ratio was then investigated. Table 12 reports the results of reactions between Na_2MoO_4 and excess amino acids together with the reactions in stoichiometric conditions (M/L = 2 : 1) for comparison.

Tab. 12. Reactions of Q_2MoO_4 (Q = Na, NH_4) and amino acids with different starting molar ratios (M/L) and molybdenum concentrations (room temperature, pH = 2 (HNO_3))

M/L	2 : 1		1 : 1		1 : 2		1 : 13.7	
aaH molar excess	no excess		2		4		27.4	
[Mo]$_0$	0.1		0.06		0.02-0.06*		0.01	
Amino acid	Yield	Solid formation	Yield	Solid formation	Yield	Solid formation	Yield	Solid formation
GlyH	90 %	after 25 min			78 %	after 10 min	70 %	after 5 min
PheH	90 %	after 2.5 h			84 %	after 3 h		
LeuH	77 %	from the residue after complete evaporation	74 %	only after concentrating up to [Mo] = 0.1	93 %	after 3.5 h		
MetH	82 %	after 25 min			74 %	after 30 min		
ProH	73 %	after 25 min			68 %	after 5 min		

* [Mo]$_0 \approx$ 0.06 for LeuH and PheH; [Mo]$_0 \approx$ 0.03 for GlyH and MetH; [Mo]$_0 \approx$ 0.02 for ProH

The product obtained from each reaction was $Mo_2O_4(OH)_4(aaH)$. The presence of excess amino acid did not significantly decrease the yield, compared to the stoichiometric reaction (e.g. with a 27-fold molar excess of glycine, $Mo_2O_4(OH)_4(GlyH)$ was obtained in 70 % yield compared to 90 % in stoichiometric conditions). The amino acid remained in solution was isolated as

[aaH$_2$]NO$_3$ from the filtered solution. Thus the conditions of Mo$_2$O$_4$(OH)$_4$(aaH) formation may be enriched by the following considerations:

- Even in excess of amino acid, the product characterized by a Mo/aaH molar ratio of 2 is the only one that separates as a solid

- The presence of excess amino acid reduces the yield of Mo$_2$O$_4$(OH)$_4$(aaH) only to a minimum extent. Since [aaH$_2$]NO$_3$ was isolated, it is probable that the amino acid in excess remains in solution as a free ligand

A pH change was not observed in reactions carried out with excess amino acid, while, in stoichiometric conditions, the pH of the solution significantly increased following the formation of Mo$_2$O$_4$(OH)$_4$(aaH) (see table 10). This could be due to the buffering effect of the excess of amino acid in solution, since the pKa value of α-ammonium acids is around 2.[78]

It is interesting to note that the presence of excess amino acid reduced the time interval necessary for the formation of Mo$_2$O$_4$(OH)$_4$(aaH), compared to the reaction in stoichiometric conditions.[k] In particular, the excess of L-leucine had a very significant effect on the formation of Mo$_2$O$_4$(OH)$_4$(LeuH). As reported in table 12, complex **3** was not obtained at room temperature from a solution with [Mo]$_0$ = 0.1 in stoichiometric conditions and it was obtained in 77 % yield only from the residue after complete evaporation of the solvent. Instead, with a 2-fold molar excess of L-leucine (M/L = 1 : 1), it was sufficient to concentrate up to [Mo] = 0.1 to observe the formation of Mo$_2$O$_4$(OH)$_4$(LeuH) with a 74 % yield. On the other hand, complex **3** was obtained almost quantitatively (93 %) after only 3.5 hours from a reaction mixture with [Mo]$_0$ = 0.06 but with a four-fold molar excess of amino acid (M/L = 1 : 2).

Therefore, some reactions were carried out to evaluate the effect of temperature on the formation of Mo$_2$O$_4$(OH)$_4$(aaH) at pH = 2. Table 13 reports the outcome of these reactions.

Compound Mo$_2$O$_4$(OH)$_4$(PheH) was obtained quantitatively both at room temperature and at 70 °C. In this case, the increase in temperature did not affect the selectivity and had the sole consequence of reducing the time interval preceding the formation of the product. Indeed, by combining the accelerating effects of heating at 70 °C and the excess of amino acid, Mo$_2$O$_4$(OH)$_4$(PheH) started to form after 1.5 hours, compared to 2.5 hours at room temperature and under stoichiometric conditions.[k]

A different situation was observed with L-leucine. Compound **3** was not obtained either at room temperature (28 hours) or after heating to 70-80 °C or after cooling to 4 °C from a pH = 2 reaction mixture with a four-fold excess of L-Leucine and [Mo]$_0$ = 0.04. It was only obtained when

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k   It is necessary to consider that the reactions in excess of ligand (table 13) and at different temperatures (table 14) were carried out in more dilute solutions. The reduction of time was partially or sometimes totally offset by dilution (e.g. see the reactions with PheH in table 13).

Tab. 13. Reactions of Q_2MoO_4 (Q = Na, NH_4) and amino acids with a different thermal treatment (M/L = 1 : 2, pH = 2 (HNO_3), initial [Mo] = 0.04)

Amino acid	Thermal treatment	$Mo_2O_4(OH)_4(aaH)$ Yield	Solid formation
PheH	room temperature	97 %	after 2 hours
	70 °C	101 %	after 1.5 hours
LeuH	RT for 19 h, then 70 °C for 2 h, then 4 °C for 17 h	63 %	only after concentrating up to [Mo] = 0.08
	RT for 28 h, then 80 °C for 2 h, then 4 °C for 10 h	91 %	only after concentrating up to a very small volume

the solution was concentrated - with a higher yield from a lower volume (see table 13). However, when the reaction was performed with $[Mo]_0 = 0.06$, the other experimental conditions being the same, $Mo_2O_4(OH)_4(LeuH)$ was obtained in 93 % yield only after 3.5 hours at room temperature (see table 12, 4th column). It seems unlikely that a soluble precursor complex was formed in both cases and then it precipitated as $Mo_2O_4(OH)_4(LeuH)$ when $[Mo]_0 = 0.06$ at room temperature but remained soluble in a reaction mixture with $[Mo]_0 = 0.04$ even after 10-17 hours at 4 °C. It may be assumed instead that the initial concentration of the reactants has a considerable effect on the rate of formation of $Mo_2O_4(OH)_4(LeuH)$ as a solid.

Finally, some reactions were carried out in D_2O to identify any complexes in solution by NMR spectroscopy. A solution of amino acid (LeuH, PheH, ProH or $(NMe_2)PheH)$) and $(NH_4)_2MoO_4$ (M/L = 1 : 2, $[Mo]_0 \approx 0.08$) was acidified with HNO_3 until pH = 2 and the usual $Mo_2O_4(OH)_4(aaH)$ product was obtained almost immediately (after 1 hour with L-leucine). ^{1}H and ^{13}C-NMR spectra of the solution, after $Mo_2O_4(OH)_4(aaH)$ formation, showed only one group of sharp signals, both in ^{1}H and ^{13}C spectra. These were identical to the ones found for a pH = 2 solution of amino acid (LeuH and ProH) or consistent with those expected for the amino acid in solution at that pH value (PheH, $(NMe_2)PheH)$. In addition, ^{1}H and ^{13}C spectra of the pH = 2 solution of L-leucine and $(NH_4)_2MoO_4$, soon after its preparation (thus before $Mo_2O_4(OH)_4(LeuH)$ formation) were also identical to the ones found for a pH = 2 solution of L-leucine.

The conclusions that might be drawn are as follows. Even in the presence of excess amino acid:

- No molybdenum-amino acid complex is present in the reaction mixture *after* the formation of $Mo_2O_4(OH)_4(aaH)$ - that is, the amino acid in excess remains uncomplexed in solution. Alternatively, if the rate of exchange between the free and the complexed ligand is much greater than the NMR timescale,[192] any complex in solution has NMR signals very close (and so indistinguishable) from those of the free amino acid at that pH.

- No molybdenum-amino acid complex is present in the reaction mixture *before* the

formation of $Mo_2O_4(OH)_4(LeuH)$. This does not exclude that any complex is present in solution immediately before the formation of **3** and of the other complexes as well. In other words, compounds **1-6**, isolated as solids, may have a soluble precursor species with a short lifetime.

As previously stated, the outcome of the reactions, for each amino acid, was not heavily influenced by the different molybdate used (see table 10). The only exception was the behaviour of L-leucine towards $(NH_4)_6Mo_7O_{24}$. Table 14 shows a summary of the reactions performed.

Tab. 14. Reactions of $(NH_4)_6Mo_7O_{24}$ and L-leucine with different thermal treatments and M/L molar ratios (pH = 2 (HNO$_3$), initial [Mo] = 0.07-0.13)

M/L molar ratio	2 : 1	2 : 1	1 : 2
Temperature	room temperature for 24 hours, then 50 °C for 4.5 hours	refluxing conditions	room temperature
Product obtained	$Mo_2O_4(OH)_4(LeuH)$	$MoO_3 \cdot H_2O$	$Mo_2O_4(OH)_4(LeuH)$
Yield	26 %	58 %	22 %
Solid formation	after 4.5 hours (at 50 °C)	after 2 hours	after 2 hours
Filtered solution	dark blue, pH = 2.4	colourless, pH = 2.4	pale light blue, pH = 2.0

Compound $Mo_2O_4(OH)_4(LeuH)$ did not form after 24 hours at room temperature in a stoichiometric reaction mixture and it was obtained in a low yield (26 %) only after heating at 50 °C for 4.5 hours. But in the meantime, before heating, the initially colourless reaction mixture gradually became dark blue. GC-MS revealed the presence of CO_2 and 3-methylbutirronitrile. The two products correspond to the oxidation and decarboxylation of L-leucine and might explain the blue colour as due to the reduction of Mo(VI) to Mo(V).[193] Reaction (14) represents the semi-reaction of oxidation.

$$+ CO_2 + 4H^+ + 4e^- \qquad (14)$$
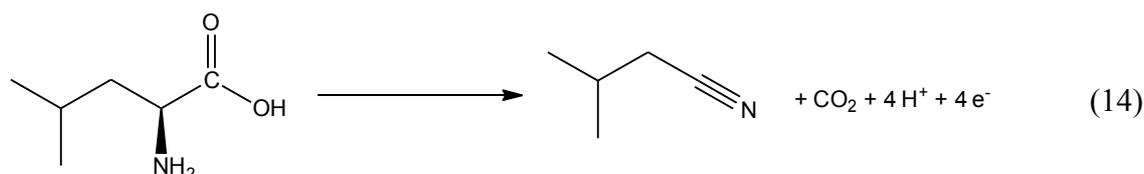
The redox reaction became slower than the formation of $Mo_2O_4(OH)_4(LeuH)$ in a reaction mixture with excess L-leucine (M/L = 1 : 2) at room temperature. In this case, complex **3** was obtained after 2 hours, although in a low yield (22 %), from a pale blue solution.

The selectivity was completely different when a pH = 2 solution of $(NH_4)_6Mo_7O_{24}$ and L-leucine (M/L = 2 : 1) was refluxed. The energy supplied to the system did not promote either the redox reaction and the formation of $Mo_2O_4(OH)_4(LeuH)$ but led to the precipitation of $MoO_3 \cdot H_2O$ in good yield. A solid that is composed of $Mo_2O_4(OH)_4(LeuH)$ and $[LeuH_2]NO_3$ was obtained by concentrating the filtered colourless solution to a small volume.

Section 3.2 – pH monitoring during the formation of $Mo_2O_4(OH)_4(GlyH)$

As noted in the previous section, the formation of $Mo_2O_4(OH)_4(aaH)$ takes place after a certain interval of time and causes an increase in pH. This time interval depends strongly on the type and on the molar excess of the amino acid used but also on the initial concentration of molybdenum.

This section describes the formation of $Mo_2O_4(OH)_4(GlyH)$, under different experimental conditions, by monitoring the variation of pH in time.

A sodium molybdate solution and a glycine solution were acidified with HNO_3 until pH = 2.00, mixed and stirred at room temperature. This was repeated with different M/L molar ratios and molybdenum concentrations. The time profiles of pH for the three reactions (named **I**, **II** and **III**) are displayed in figure 35 and other features are reported in table 15.

Tab. 15. Formation of the glycine complex in various experimental conditions with pH monitoring

Reaction	Mo/GlyH molar ratio	$[Mo]_0$	Induction period	Interval of pH change	Lowest pH	Final pH	$Mo_2O_4(OH)_4(GlyH)$ Yield
I	1.0	$5.00 \cdot 10^{-2}$	15 min	57 min	2.05	2.17	84 %
II	1.6	$1.00 \cdot 10^{-1}$	22 min	96 min	2.08	2.48	88 %
III	2.0	$6.66 \cdot 10^{-2}$	39 min	93 min	2.08	2.36	87 %

Induction period = initial interval of time during which the pH is stable or decreases slightly
Interval of pH change = interval of time during which the pH increases
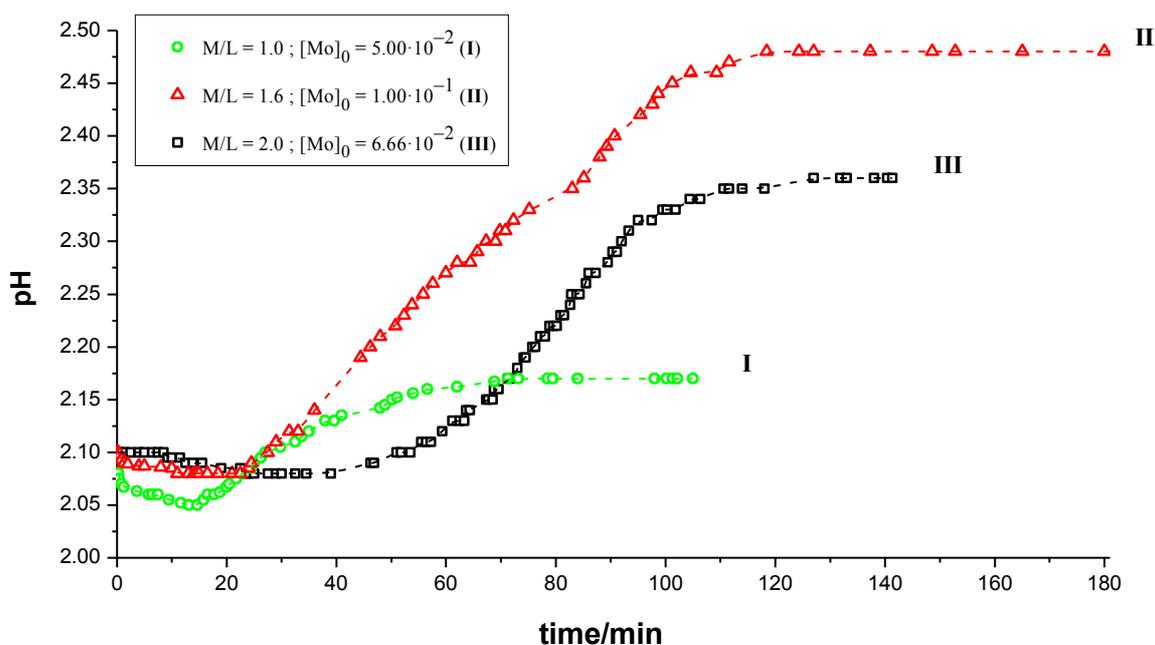
Fig. 35. The profile of pH vs. time for reactions of Na_2MoO_4 with glycine with different M/L ratios and $[Mo]_0$

The variation of pH over time can be divided into three parts:

- A first one in which the pH remains almost constant

- A second one in which the pH increases, at first almost linearly and then it gradually stabilizes to a constant value

- A final one in which the pH reaches a constant value

When the pH started to increase, the appearance of a colourless solid was observed. Hence, it can be assumed that the formation of this product ceased when the pH turned constant with time. The solutions were filtered and $Mo_2O_4(OH)_4(GlyH)$ was recovered in high yield (84–87 %).

The formation of **1** at pH = 2 is accompanied by an increase in the pH that is more or less marked depending on the initial concentration of molybdenum and on the excess of amino acid. The change of pH is less evident in reaction **I** (M/L = 1 : 1) with respect to reaction **III** (M/L = 2 : 1), for the aforementioned buffer effect due to the excess of amino acid. Instead, the pH jump is higher in reaction **II** ($[Mo]_0 = 0.10$) rather than in reaction **III** ($[Mo]_0 = 0.07$), despite a 1.25-fold molar excess of glycine in reaction **II**.

This consumption of H^+ ions is small in any case and does not account for the four moles of H^+ expected for the reaction (15). This suggests that the formation of $Mo_2O_4(OH)_4(GlyH)$ takes place mainly from neutral reactive species in solution while only in a small part from anionic species.

$$4\,H^+ + 2\,[MoO_4]^{2-} + GlyH \longrightarrow Mo_2O_4(OH)_4(GlyH) \tag{15}$$

The time interval during which the pH increased was about 95 minutes in stoichiometric conditions (reaction **III**) and with a M/L ratio of 1.6 (reaction **II**), whereas it was well reduced (ca. 60 minutes) in the presence of a two-fold excess of glycine (reaction **I**).

Furthermore, a direct correlation may be found between the excess of amino acid and the interval of time before the formation of the solid (and the simultaneous increase in pH). This "*induction period*"[194] versus the M/L ratio for reactions **I**,**II** and **III** is reported in figure 36.
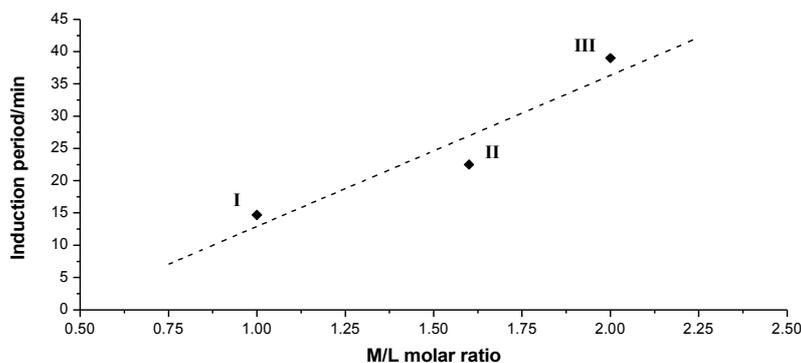
Fig. 36. The correlation between induction period and M/L molar ratio in reactions **I**, **II** and **III**.

As already noted, this induction period is in some way connected to an interaction between amino acid and molybdenum, since its duration depends strongly on the amino acid used. The dependence of this time interval on the amount of amino acid in solution strengthens this hypothesis.

The formation of $Mo_2O_4(OH)_4(GlyH)$ was further studied by titrating with HNO_3 an aqueous solution of sodium molybdate and glycine in stoichiometric ratio. Figure 37 shows the values of pH reached soon after each HNO_3 addition and remained stable in the next 20-40 minutes. The amount of acid added is expressed as H^+/glycine molar ratio.

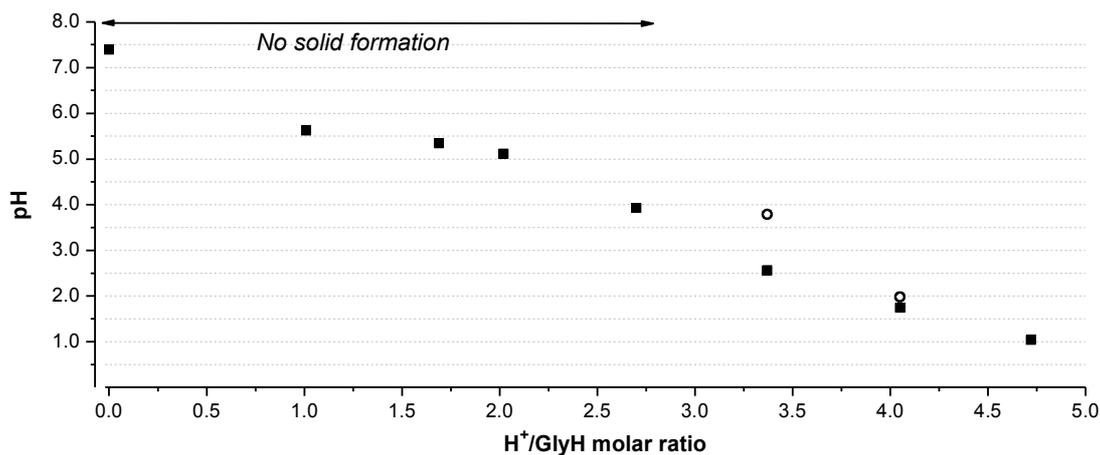**Fig. 37.** Titration of an aqueous solution of Na_2MoO_4 and glycine in a 2 : 1 ratio with HNO_3. The filled squares represent the pH value measured after 20-40 minutes from each HNO_3 addition (pH = 3.93 for H^+/GlyH = 2.70 was stable up to 14.5 h). The empty circles represent the final pH value after the formation of $Mo_2O_4(OH)_4(GlyH)$

The formation of a solid was not observed and the pH remained constant over time for each addition up to a H^+/GlyH molar ratio of 2.70. When the addition of HNO_3 led to H^+/GlyH molar ratio of 3.37, the variation of pH vs. time reported in figure 38(a) was observed. The pH of the reaction mixture quickly reached a value of 2.55 (filled square in figure 37), it remained constant for ca. 30 minutes and then it began to increase with the formation of a colourless solid. After ca. 320 minutes from the beginning of the reaction, a stable value of pH = 3.93 was reached (empty circle in figure 37). When the H^+/GlyH molar ratio was raised to 4.05, an increase in pH was observed, thus indicating further formation of product. It is interesting to note that there was no induction period (see figure 38(b)). A further addition of HNO_3 (H^+/GlyH molar ratio of 4.72), decreased the pH from 1.98 to 1.04. This value remained constant for the next 60 minutes, indicating no further complex formation.

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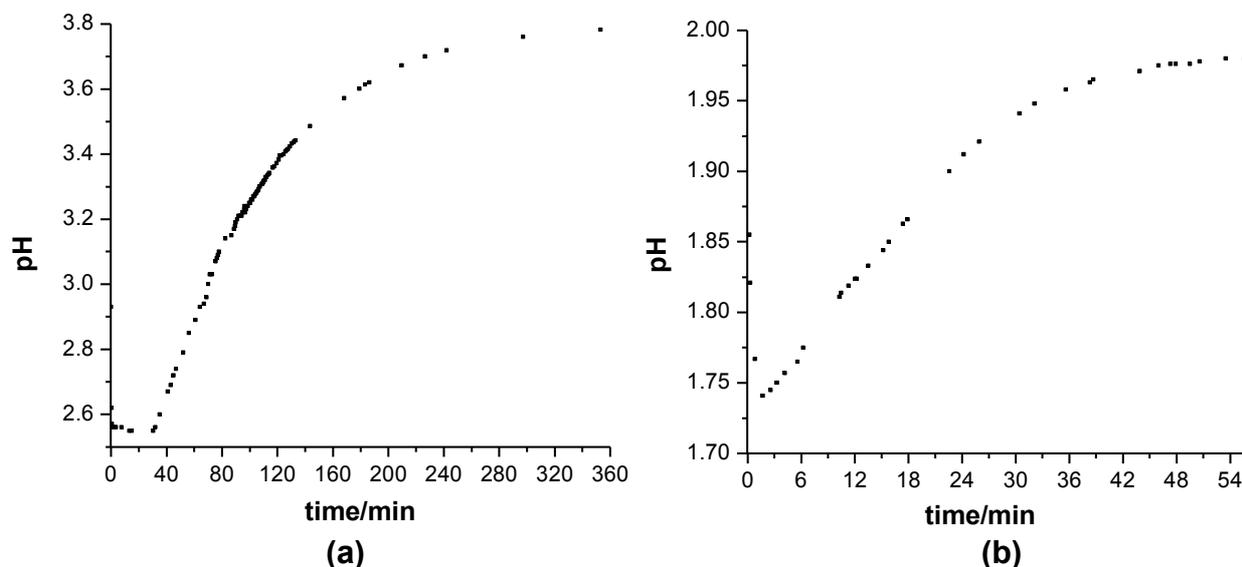
Fig. 38. The profile of pH vs. time after reaching a H$^+$/GlyH molar ratio of 3.37 (a) and 4.05 (b)

Since the amount of HNO$_3$ added and the pH of the solution after the second and final reaction[l] are known, the number of moles of H$^+$ reacted (Δn_{H^+}) can be calculated by equation (16).[m] By knowing the amount of product isolated (m) and its molecular weight (M), the ratio between the moles of H$^+$ reacted and the moles of Mo$_2$O$_4$(OH)$_4$(GlyH) obtained can be calculated by equation (17).

$$\Delta n_{H^+} = V_{HNO_3} \cdot c_{HNO_3} - V_{sol} \cdot 10^{-pH_{sol}} \tag{16}$$

$$\nu_{H^+} = \frac{\Delta n_{H^+}}{m/M} \tag{17}$$

The value obtained for the ν_{H^+} coefficient is 4.43, which is very close to the stoichiometric coefficient of H$^+$ required for the formation reaction proposed (18). However, through this experiment, there is no way to exclude or confirm the possibility of a condensation reaction (19), nor to measure its extent.[n]

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l   This quantity is indicated as pH$_{sol}$ in (14) and it corresponds to the empty circle for H$^+$/GlyH = 4.05 in figure 37

m   It is assumed that the final volume of reaction mixture (V$_{sol}$) is the sum of the initial solution volume and the volume of HNO$_3$ added. The value of Δn_{H^+} obtained with equation (16) is probably overestimated since it does not consider any possible equilibrium, established after the formation of Mo$_2$O$_4$(OH)$_4$(GlyH), which may involve H$^+$, reducing its concentration. Examples are the protonation of the unreacted glycine or molybdate (shown in figure 39). Nevertheless, since the formation of Mo$_2$O$_4$(OH)$_4$(GlyH) was almost quantitative (88 % yield) and the reaction was carried out under stoichiometric conditions, the value of Δn_{H^+} may be not too biased
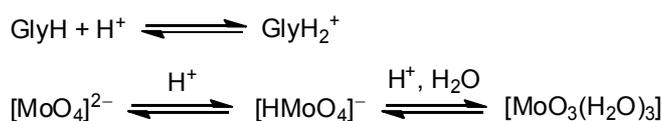
Fig. 39. Protonation equilibria of glycine and molybdate

n   Indeed, if the oxo-bridged polymeric formulation for the reaction product is considered, {Mo$_2$O$_4$(OH)$_2$(GlyH)(μ-O)}$_n$, a yield of 92 % (instead of 88 %) and a ν_{H^+} coefficient of 4.23 (instead of 4.43) are obtained.

$$4\,H^+ + 2\,[MoO_4]^{2-} + GlyH \longrightarrow Mo_2O_4(OH)_4(GlyH) \qquad (18)$$

$$n\,Mo_2O_4(OH)_4(aaH) \longrightarrow \{Mo_2O_4(OH)_2(aaH)(\mu\text{-}O)\}_n \cdot H_2O + (n\text{-}1)\,H_2O \qquad (19)$$

In a final experiment, an aqueous solution of sodium molybdate was titrated with HNO_3. After each addition of HNO_3, the pH reached the equilibrium value in less than a minute and then remained constant over time. The typical molybdate titration curve[47] was obtained (see figure 40). When a pH = 2 solution was obtained, the stoichiometric amount of solid glycine was added (M/L = 2 : 1). The profile of pH vs. time obtained is reported in figure 41.
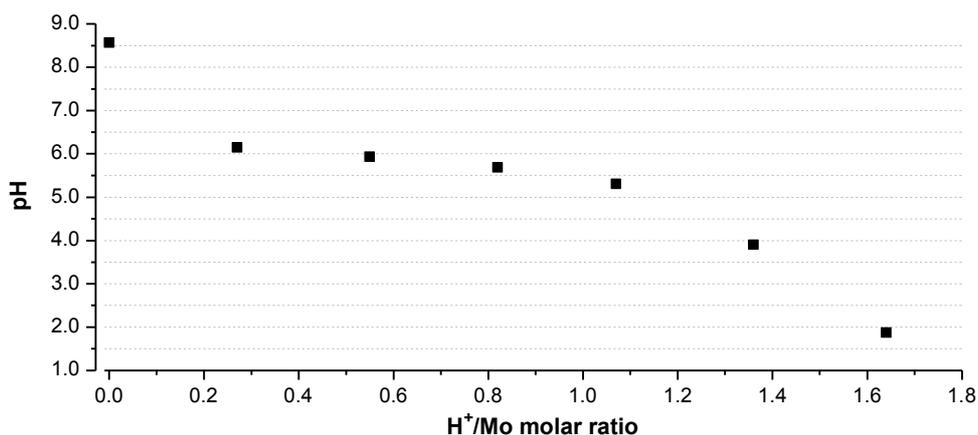
Fig. 40. Titration of a 0.2 M solution of Na_2MO_4 with HNO_3
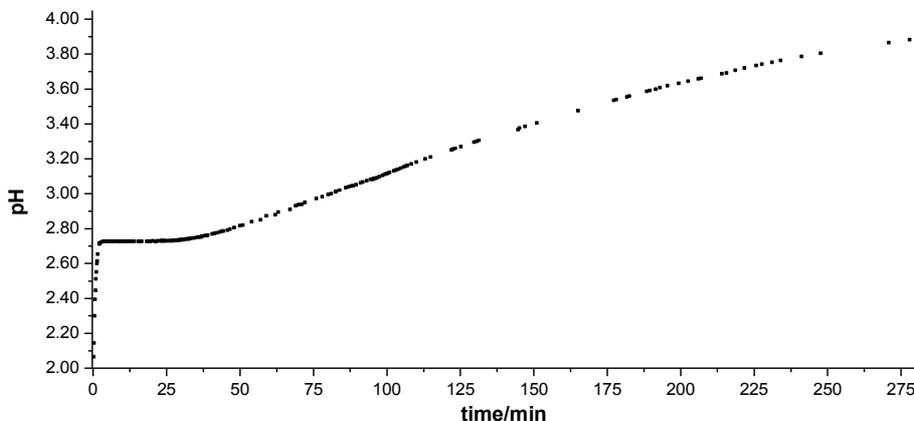
Fig. 41. The profile of pH vs. time after the glycine addition (a final pH value of 4.17 was reached after ca. 6 hours)

Glycine was soon dissolved and the pH rose up to 2.72 (probably due to the protonation equilibrium of glycine) and remained constant in time. After ca. 30 minutes a solid was formed while pH began to rise. The reaction was very slow: the pH took up about 6 hours to reach the final value (pH = 4.17).

Compound $Mo_2O_4(OH)_4(GlyH)$ was obtained in a low yield (41 %). This was so because the H^+/Mo molar ratio was lower (1.64 instead of 2) but also because the H^+ consumption did not proceed beyond pH $\approx$ 4.2.

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Section 3.3 - Solid state NMR characterization

Given that the synthesized compounds were insoluble in most of the common solvents (see section 3.6), isotropic ^{13}C chemical shifts in solid-state NMR spectroscopy were used to characterize the amino acidic ligands.

As can be seen in table 16, ^{13}C CP-MAS spectra of $Mo_2O_4(OH)_4(aaH)$ complexes showed a single set of chemical shifts attributable to the amino acid for glycine, L-phenylalanine, L-leucine and *N,N*-dimethyl-L-phenylalanine, two sets for L-methionine and 3 sets for L-proline. Such splitting in solid-state ^{13}C spectra might be due to a different molecular environment (e.g. different hydrogen bonding interactions or different molecular conformation) or to a different crystallographic environment.[195] Spectra of complexes **1-6** showed quite narrow signals (e.g. the spectrum of **3** in figure 42) thus indicating that the samples were poorly crystalline but not amorphous.[196]
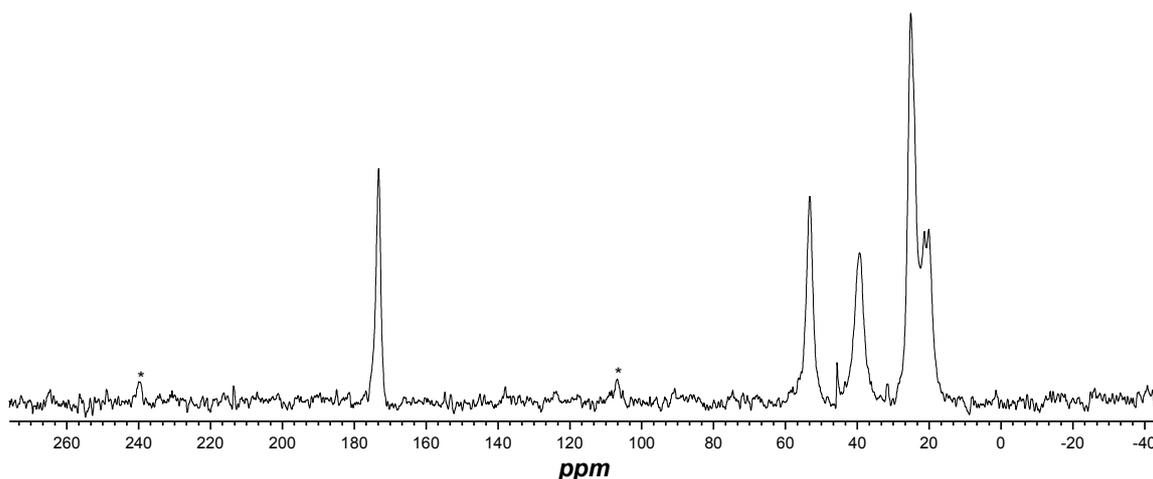
Fig. 42. ^{13}C CP-MAS spectrum of $Mo_2O_4(OH)_4(LeuH)$

The NMR characterization is based on a comparison with ^{13}C solid state spectra of amino acids and their salt derivatives obtained by deprotonation with NaOH or protonation with HNO_3. In turn, the trend of chemical shift as a function of the degree of protonation, observed in the solid state, is compared with the behaviour in aqueous solution, which is known in the literature.[197-199]

^{13}C and ^1H chemical shift values of organic molecules in solution are influenced by the extent of their ionization. For acids and bases in aqueous solutions, chemical shifts depend on the protonation equilibria. The behaviour of ^{13}C chemical shift as a function of pH has been reported for a large number of amines, carboxylic acids, amino acids and small peptides and has been used for accurate determination of pK_a values.[197,199,200]

Tab. 16. ^{13}C CP-MAS chemical shifts of $Mo_2O_4(OH)_4(aaH)$ complexes

Compound	δ/ppm
$Mo_2O_4(OH)_4(GlyH)$	172.0 (CO); 41.3 (CH_2)
$Mo_2O_4(OH)_4(PheH)$	172.6 (CO); 134.5 (Ph); 133.6 (Ph); 132.5 (Ph); 129.6 (Ph); 57.3 (CH); 35.6 (CH_2)
$Mo_2O_4(OH)_4(LeuH)$	173.2 (CO); 53.3 (CHN); 39.3 (CH_2); 25.1 ($CHMe_2$); 21.3 (CH_3); 20.1 (CH_3)
$Mo_2O_4(OH)_4(MetH)$	174.4 (CO); 171.8 (CO); 54.7 (CH); 31.5 (CH_2CH); 30.4 (CH_2CH); 28.7 (SCH_2); 15.3 (SCH_3); 14.4 (SCH_3); 12.4 (SCH_3)
$Mo_2O_4(OH)_4(ProH)$	176.0 (CO); 175.2 (CO); 173.5 (CO); 65.0 (CH); 61.0 (CH); 49.7 (CH_2N); 47.3 (CH_2N); 46.9 (CH_2N); 30.2 (CH_2CH); 29.4 (CH_2CH); 26.2 ($CH_2(CH_2)_2$); 25.8 ($CH_2(CH_2)_2$); 23.7 ($CH_2(CH_2)_2$)
$Mo_2O_4(OH)_4((NMe_2)PheH)$	171.6 (CO); 140.9 (Ph); 130.8 (Ph); 128.9 (Ph); 127.8 (Ph); 69.9 (CH); 42.0 (NCH_3); 36.6 (NCH_3); 30.4 (CH_2)

The *protonation shift* (20) is defined as the chemical shift difference, for a specified nucleus, between the protonated form of the molecule and the deprotonated one.[200]

$$\Delta_c = \delta_{HA^+} - \delta_A \qquad (20)$$

A negative value indicates an upfield shift (shielding) on protonation and vice versa. Amino acids, having two ionizable groups with very different pK_a, will have 2 protonation shifts, related to the protonation of the amino group and the carboxylate group, as indicated in (21).

$$H_2NCH(R)COO^- + 2H^+ \rightleftharpoons {}^+H_3NCH(R)COO^- + H^+ \rightleftharpoons {}^+H_3NCH(R)COOH \qquad (21)$$

It has been observed that protonation of either a carboxylate or an amine leads to upfield shifts of ^{13}C resonances and downfield shifts of ^{1}H resonances. The observed shifts decrease monotonically with the number of bonds separating a nucleus from the protonation site.[197] The direction of increased shielding of ^{13}C nuclei on protonation is not easily explained, since it would seem to imply an increase in charge density on carbon atoms in each protonation step.[201-202] However, the chemical shift is influenced not only by a *diamagnetic contribution* (σ_d), which is proportional to electron density, but also by a *paramagnetic contribution* (σ_p), which depends on both electron density and the degree of mixing of excited electronic states.[203] Freedman et al.[198] suggested that, although some bond polarization occurs, the observed shielding on protonation is often the result of an increase in excitation energy that more than compensates for a decrease in electron density.

Average ^{13}C protonation shifts for α-amino acids are reported in table 17.[199]

Tab. 17. Average protonation shifts observed for amino acids[199]

Carbon atom	Carboxylic carbon	α-carbon	β-carbon	N-methyl groups*	farther out carbons
Δ_c/ppm −NH₂ protonation	−8.3	−1.4 (CH) −3.1 (CH₂)	−3.2 (CH) −4.4 (CH₂)	−1	small, upfield shifts (0.0 to −1.0)
Δ_c/ppm −COO⁻ protonation	−2.6	−1.9	−0.7	+0.3	

* Evaluated only for *N,N*-dimethylglycine and sarcosine (*N*-methylglycine)

The titration of the amino group affects both the carbonyl carbon and the β-carbon more strongly than the nearby α-carbon. In contrast, the protonation of the carboxylic moiety leads to similar and much smaller protonation shifts for the α-carbon and the carboxylic carbon.[198] The ^{13}C chemical shift of *N*-methyl groups seems to be influenced to a lesser extent by the ionization of the molecule.

To compare this trend with that in the solid state, it was necessary to prepare compounds containing the amino acids of interest in the deprotonated [H₂NCH(R)COO⁻] or protonated [⁺H₃NCH(R)COOH] forms.

Many addition compounds of amino acids and inorganic acids have been structurally characterized.[204] These compounds may be indicated with the general formula (aaH)ₙ·HA. The crystal structure of 1 : 1 adducts with nitric acid is known for glycine,[205] DL-phenylalanine ,[206] L-methionine,[207] L-[208] and DL-leucine[209] (reported in figure 43). Only a 2 : 1 adduct is known for L-proline and HNO₃,[210] while compounds with 2 : 1[211] and 4 : 1[212] stoichiometry are known for L-phenylalanine.
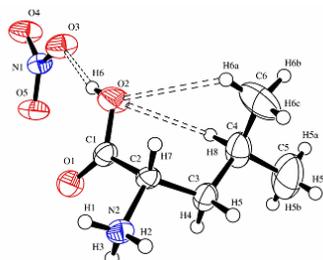
Fig. 43. The asymmetric unit of DL-leucinium nitrate.[209] Dashed lines represent hydrogen bonds

Table 18 reports carbon-oxygen distances for the carboxylic group of some amino acids and their 1 : 1 adducts with nitric acid. In the latter compounds, the two C−O distances of the carboxylic fragment are quite different, suggesting the presence of different bond orders. In view of the protonation of the amino group, these adducts are actually the ammonium salt of the amino acid and can be described with the general formula [aaH₂]NO₃. Amino acids instead exist as zwitterions in the solid state, with a protonated ammonium group and a deprotonated carboxylate, as remarked from the fact that carbon-oxygen distances are identical.

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Tab. 18. C–O bond lengths in some amino acids and corresponding amino acid-nitric acid 1 : 1 adducts

Compound	$d_{C-O1}/Å$	$d_{C-O2}/Å$	Ref.	Compound	$d_{C-O1}/Å$	$d_{C-O2}/Å$	Ref.
Glycine (α polymorph)	1.252	1.255	[213]	Glycine nitrate	1.205	1.324	[205]
L-methionine*	1.254 1.268	1.230 1.246	[214]	L-methionine nitrate*	1.194 1.199	1.299 1.307	[207]
L-leucine*	1.258 1.263	1.255 1.252	[215]	L-leucine nitrate*	1.197 1.158	1.240 1.391	[208]

*two crystallographically independent molecules in the asymmetric unit

The only structurally characterized compound, with 1 : 1 stoichiometry, obtained from an amino acid and an alkali hydroxide is lithium glycinate.[216] This compound contains glycinato anions ($H_2N-CH_2-COO^-$) and Li^+ cations (see figure 44). Sodium glycinate[217,218] and sodium DL-methioninate[219] have also been synthesized and spectroscopically characterized.
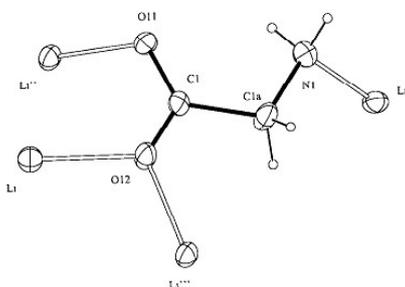
Fig. 44. Structure of the glycinate coordination in Li[Gly][216]

Some amino acid nitrates, [aaH$_2$]NO$_3$, and sodium amino acidates, Na[aa], were then prepared. Glycine, L-phenylalanine, L-leucine and L-methionine nitrates were obtained in a crystalline state by slow evaporation of aqueous solutions containing amino acid and nitric acid in 1 : 1 molar ratio or in excess of acid. L-methionine and *N,N*-dimethyl-L-phenylalanine sodium salts were prepared by slow evaporation of aqueous solutions containing amino acid and excess NaOH.

From the comparison of ^{13}C solid state spectra (see table 19), it may be noted that the isotropic chemical shift as a function of the degree of protonation (see figure 45) has - with some exceptions - a similar trend to that found as a function of pH in aqueous solution. In other words, protonation shifts in solution and in the solid state are similar.[o]

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o   As far as the Na[Met] to MetH protonation is concerned, a shift of −5.8 ppm for the carboxylic carbon, −2.9 ppm for the α carbon and −6.2 ppm for the β carbon are observed. By comparing the spectra of Na[(NMe$_2$)Phe] and (NMe$_2$)PheH, a shift of −5.0 ppm for the carboxylic carbon, −6.8 ppm for the α carbon, +6.0 ppm for the β carbon and substantially no shift for the nitrogen-bonded CH$_3$ groups are observed. These features are in agreement to what observed in solution for the first protonation, the only significant differences being the rather high shift for α carbon and a the high positive shift for the β carbon of *N,N*-dimethyl-L-phenylalanine. Comparing the spectra of aaH and [aaH$_2$]NO$_3$, a shift of ca. −4 ppm for the carboxylic carbon (except −1.8 for PheH), a small shift for the α-CH carbon (+0.8 to −1.5 ppm), a higher shift for the α-CH$_2$ carbon of glycine (−2.4 ppm) and a shift of ca. −2 ppm for the β carbon (except +0.4 for MetH) are observed. Again, with few exceptions, the trend observed in solution for the carboxylate protonation is qualitatively reflected.
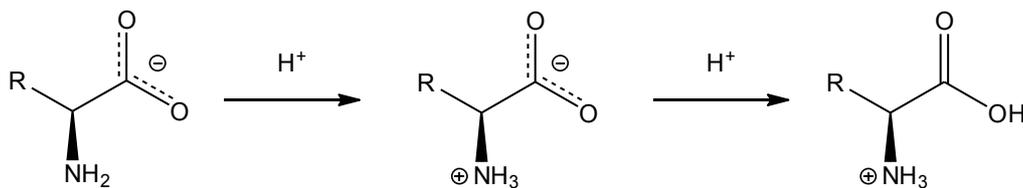
Fig. 45. Protonated, zwitterionic and deprotonated forms of an α-amino acid

Remarks on NMR spectra of Mo$_2$O$_4$(OH)$_4$(aaH) complexes

As shown in table 19, the chemical shifts for carboxylic, α and β carbons of glycine, L-leucine, L-methionine and L-phenylalanine complexes are very close to the values found for the diprotonated derivatives. The values for the α carbon are close to the zwitterionic values as well, since it has been observed that, both in solution and in the solid state, the second protonation shift is very small for this carbon atom.

Though a direct comparison can not be done, the complex of *N,N*-dimethyl-L-phenylalanine is coherent with the others with respect to the carboxylic carbon (171.6 ppm, with a shift of −1 ppm with respect to the zwitterionic amino acid); instead the α, β and *N*−CH$_3$ carbons have a positive shift of about 2.5 ppm with respect the values observed in the the zwitterion.

The NMR spectrum of the L-proline complex identifies three groups of signals for the amino acid. One of these reflects the general trend observed with the other complexes (173.5; 61.0; 46.9; 29.4; 23.7), while the other two, very close in value, are more deshielded, being close or higher (as in the case of the α-carbon) than the zwitterionic values (176.8 / 175.2; 65.0; 49.7 / 47.3; 30.2; 26.2 / 25.8).

It can be concluded that, with some exceptions, the chemical shifts observed in going from the zwitterion to the complex are similar to those observed in going from the zwitterion to the ammoniumacid nitrate. This supports the hypothesis that the amino acid is protonated on the amino group and is bonded to the metal via the carboxylate group: the complexation "mimics" the electronic effects caused by protonation and thus a similarity of shift is observed.

A correlation between solid state ^{13}C NMR isotropic chemical shift and carboxylate coordination mode has been studied for acetate ligands in tetranuclear complexes of Zinc[221] and porphyrin complexes of main group elements (Ga, In, Tl, Ge and Sn).[222] However, it is difficult to provide a general rule, as these shifts may be strongly influenced by the electronic effect of the metal centre. In absence of ^{13}C chemical shifts of carboxylate ligands bound to molybdenum(VI) complexes as a reference, it is not easy to discern the type of coordination of the carboxylate group from the NMR spectra obtained.

Tab. 19. Comparison between the ^{13}C CP-MAS chemical shifts (in ppm) of Na[aa], aaH, [aaH$_2$]NO$_3$ and Mo$_2$O$_4$(OH)$_4$(aaH)

Amino acid	Type of Carbon	Na[aa]	aaH	[aaH₂]NO₃	Mo₂O₄(OH)₄(aaH)
Glycine	CO		176.2[220] (*α polymorph*)	171.7	172.0
	Cα		43.5[220] (*α polymorph*)	41.1	41.3
L-Phenylalanine	CO		175.3	173.9 ; 173.2	172.6
	Cα		58.3 ; 56.4	56.3 ; 55.5	57.3
	Cβ		40.4 ; 37.6	37.0 ; 36.3	35.6
	Ph		135.4 ; 130.1 ; 128.4	135.2 ; 132.8 ; 132.3 ; 129.8 ; 129.3 ; 127.6 ; 127.3	134.5 ; 133.6 ; 132.5 ; 129.6
L-Leucine	CO		176.7 ; 175.8	173.9 ; 173.1	173.2
	Cα		53.8 ; 52.7	52.9	53.3
	Cβ		42.4 ; 40.6	39.2	39.3
	Cγ		24.6	24.7	25.1
	Cδ			23.3 ; 22.3 ; 21.7 ; 20.0	21.3 ; 20.1
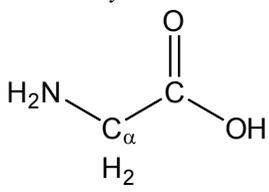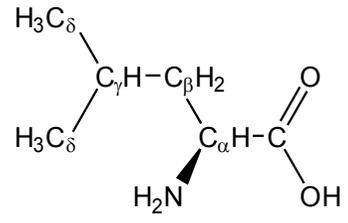
L-Methionine					
	CO	183.9 ; 181.2	176.7	173.7 ; 172.2	174.4 ; 171.8
	C_α	56.6	55.2 ; 52.1	54.6 ; 54.4	54.7
	C_β	40.1 ; 37.3	32.9 ; 32.0	32.9	31.5 ; 30.4
	C_γ	33.6 ; 31.8	31.0	30.2	28.7
	SCH_3	16.9 ; 16.5	17.3 ; 15.3	16.0 ; 15.5	15.3 ; 14.4 ; 12.4
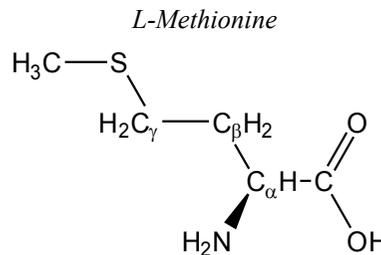
L-Methionine structure: H_3C-S, $H_2C_\gamma-C_\beta H_2$, $C_\alpha H-C$, H_2N, O, OH

L-Proline					
	CO		176.7		176.8 ; 175.2 ; 173.5
	C_α		60.6		65.0 ; 61.0
	C_β		29.6		30.2 ; 29.4
	C_γ		25.1		26.2 ; 25.8 ; 23.7
	C_δ		47.8		49.7 ; 47.3 ; 46.9

L-Proline structure: N, H, H_2C_δ, H_2C_γ, $C_\beta H_2$, C_α, C, O, OH

N,N-Dimethyl-L-phenylalanine					
	CO	178.3 ; 176.9	172.6		171.6
	C_α	73.7 ; 73.3; 72.9	66.5		69.9
	C_β	29.4	35.4		36.6
	NCH_3	42.3; 38.7; 36.0	39.0		42.0
	Ph	144.4 ; 143.8 ; 142.2 ; 133.8 ; 132.7 ; 130.6 ; 128.3 ; 126.0 ; 124.8	139.0 ; 130.6 ; 129.1 ; 127.7 ; 125.8		140.9 ; 130.8 ; 128.9 ; 127.8

N,N-Dimethyl-L-phenylalanine structure: $C_\beta H_2$, $C_\alpha H-C$, H_3C-N, CH_3, O, OH

Signal splitting for PheH, LeuH, [LeuH$_2$]NO$_3$, MetH, [MetH$_2$]NO$_3$ is due to the presence of 2 crystallographically independent molecules in the asymmetric unit. This is probably true also for Na[Met], [PheH$_2$]NO$_3$ and Na[(NMe$_2$)Phe] (3 molecules for the latter), which crystal structures are not known.

Section 3.4 - IR characterization

Figures 46-51 report the solid state IR spectra of $Mo_2O_4(OH)_4(aaH)$ compounds. The main IR absorptions of **1-6** complexes and the proposed vibrational assignments are summarized in table 20. For comparative purposes, major IR bands of uncomplexed α-amino acids used as ligands are also reported, together with vibrational assignments taken from the literature.

IR spectra of $Mo_2O_4(OH)_4(aaH)$ complexes show bands due to the amino acid ligand in the 2800-3300 cm^{-1} and 1200-1650 cm^{-1} regions whereas vibrations due to molybdenum-oxygen bonds are recognizable between 1000 and 700 cm^{-1} and in the broad band around 500 cm^{-1}. The interpretation of these spectra is reported below.
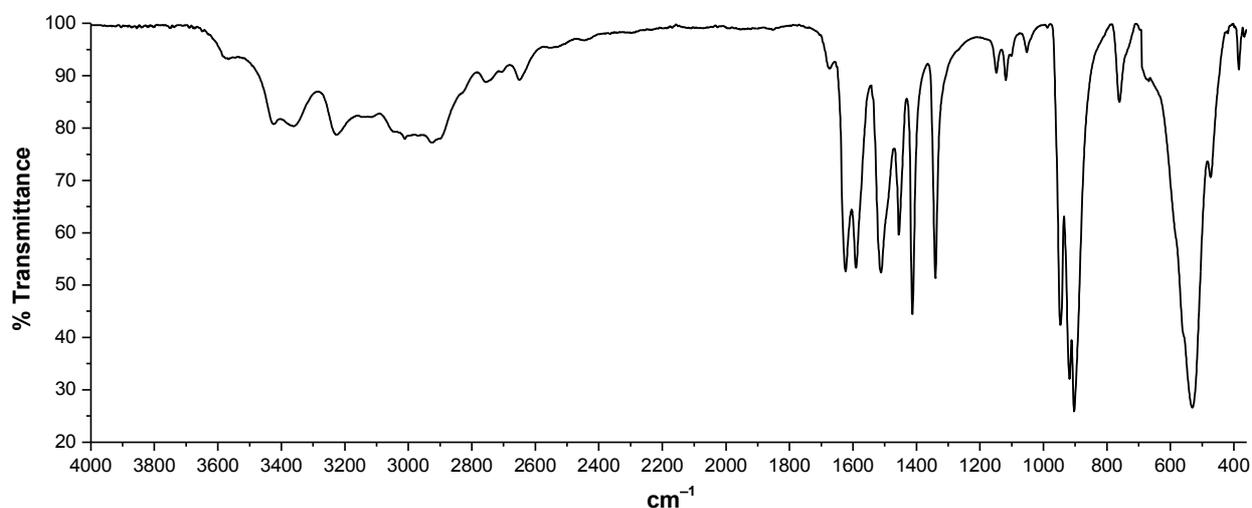
Fig. 46. Solid state IR spectrum of $Mo_2O_4(OH)_4(GlyH)$
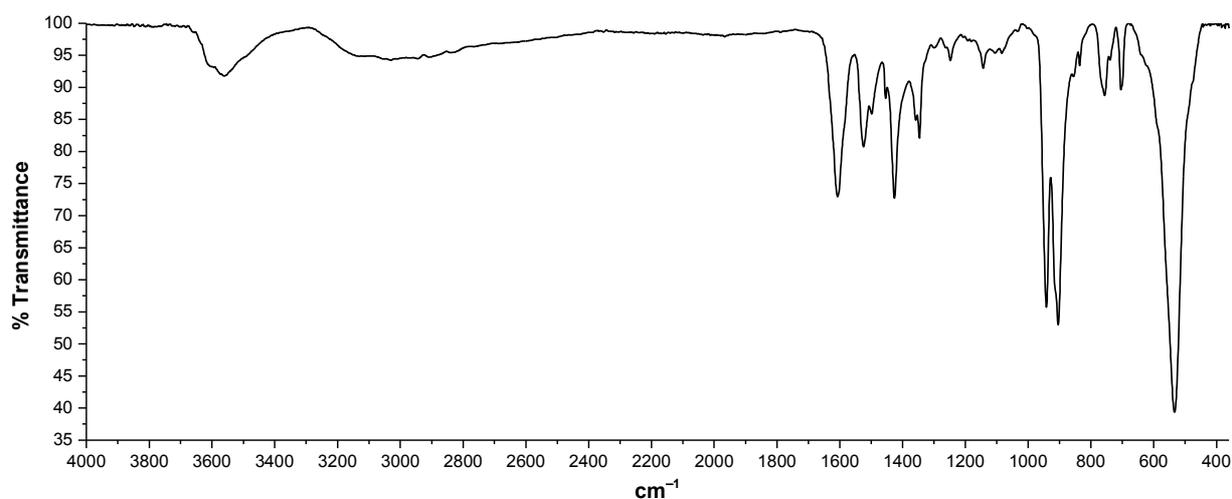
Fig. 47. Solid state IR spectrum of $Mo_2O_4(OH)_4(PheH)$

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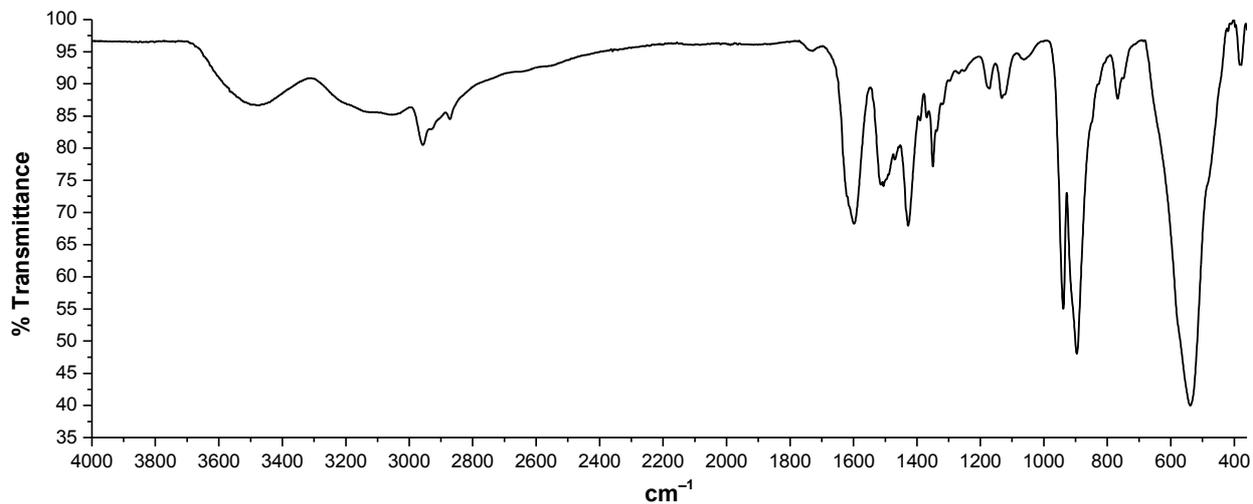
Fig. 48. Solid state IR spectrum of $Mo_2O_4(OH)_4(LeuH)$
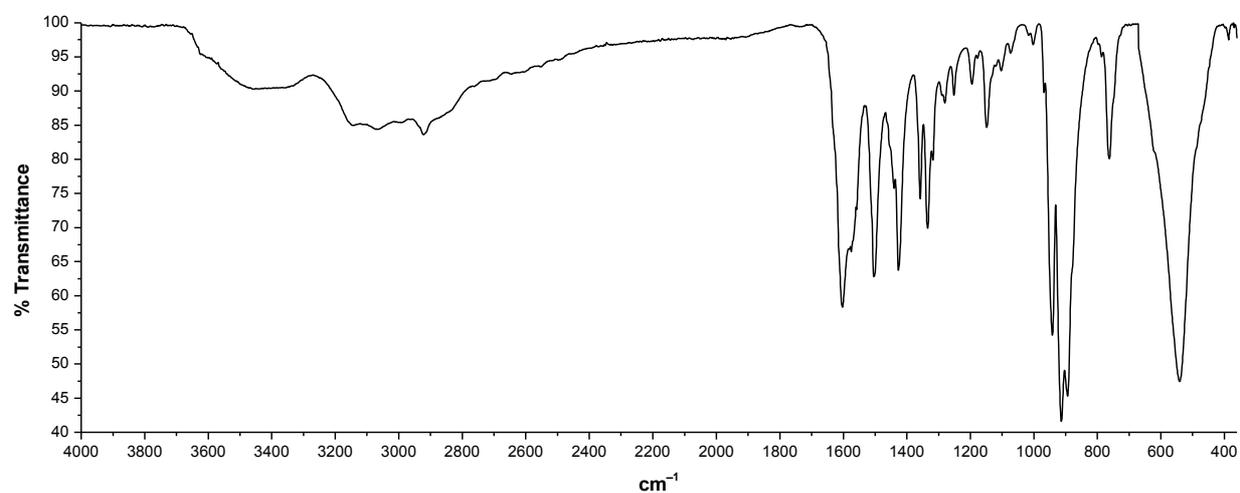
Fig. 49. Solid state IR spectrum of $Mo_2O_4(OH)_4(MetH)$
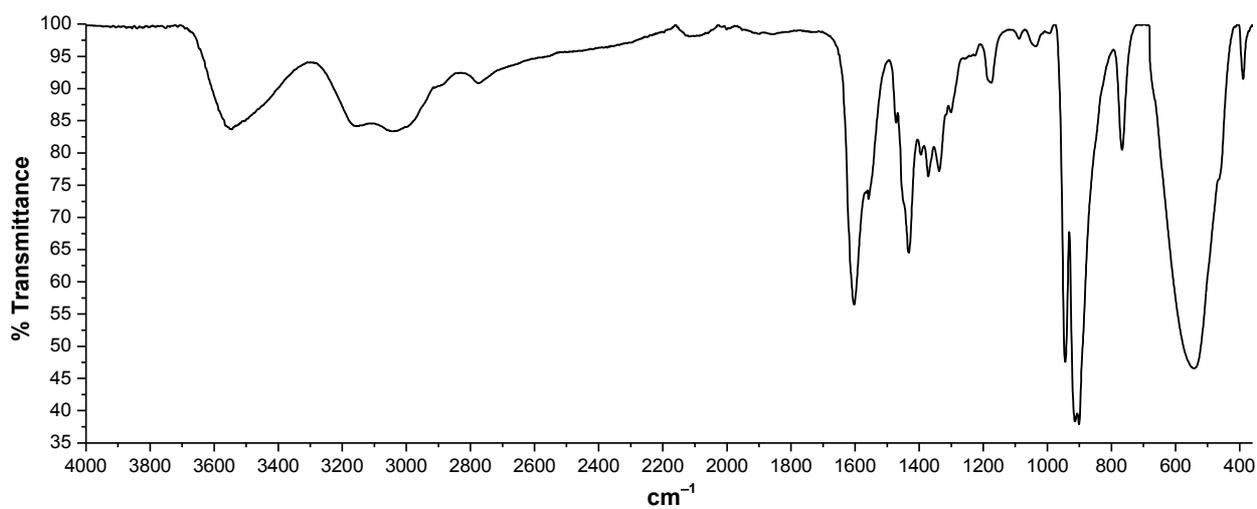
Fig. 50. Solid state IR spectrum of $Mo_2O_4(OH)_4(ProH)$

Tab. 20. Main solid state IR absorptions (in cm⁻¹) and proposed vibrational assignments for $Mo_2O_4(OH)_4(aaH)$ complexes and for the corresponding α-amino acids

| Compound | Carboxylate group | | | Ammonium group | | | | Molybdate backbone | | |
	$\nu_a(CO_2^-)$	$\nu_s(CO_2^-)$	$\Delta\nu_{a-s}$	$\delta_a(NH_3^+)$	$\delta_s(NH_3^+)$	$\nu_s(MoO_2)$	$\nu_a(MoO_2)$	$\nu_a(Mo_2O_x)$ $x = 1$ and / or 2	$\nu(Mo{-}O_{ligand})$ $+ \nu_s(Mo_2O_2)$	$\nu_s(Mo_2O)$
GlyH[223]	1610	1407	203	1580	1500					
Mo₂O₄(OH)₄(GlyH)	1623	1412	211 (+8)	1590	1511	945	917 903	760	558	474
PheH[224]	1556	1408	148	1622	1494					
Mo₂O₄(OH)₄(PheH)	1605	1425	180 (+32)	1605	1525	941	915 904	755	533	
LeuH[225]	1578	1406	172	1608	1512					
Mo₂O₄(OH)₄(LeuH)	1599	1427	172 (0)	1620	1515	938	909 897	767	538	480
MetH[226]	1582 1560	1406	165 (avg)	1608	1508					
Mo₂O₄(OH)₄(MetH)	1575	1426	149 (−16)	1601	1503	942	913 893	761	541	487
ProH[227]	1613	1404	209	δ(NH₂⁺) : 1553						
Mo₂O₄(OH)₄(ProH)	1603	1432	171 (−38)	δ(NH₂⁺) : 1559		944	913 901	767	544	461
(NMe₂)PheH	1610	1416	194	ν(N−CH₃) : 1485						
Mo₂O₄(OH)₄((NMe₂)PheH)	1626	1411	215 (+21)	ν(N−CH₃) : 1494		946	916 903	768	547	
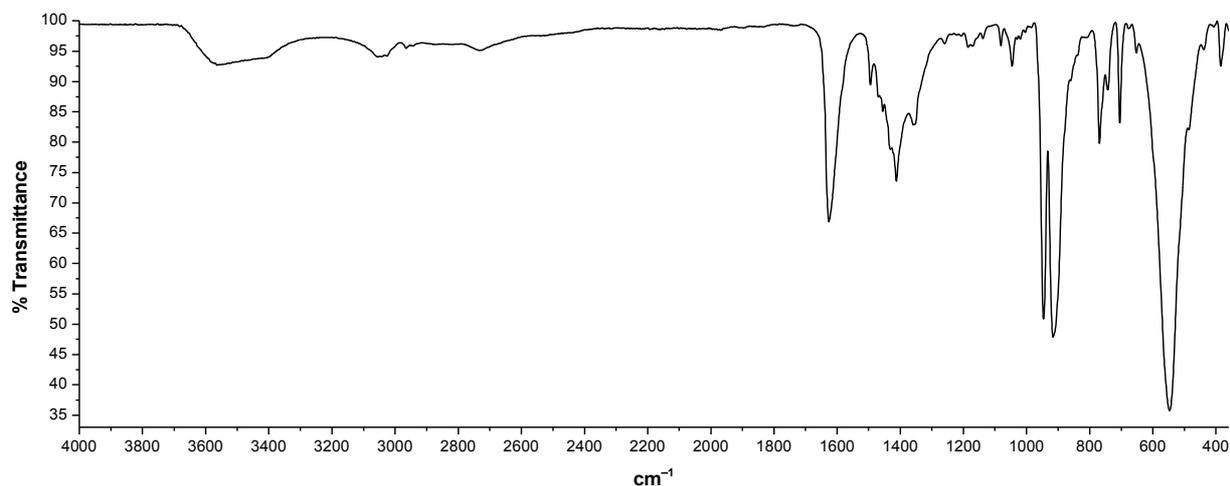
Fig. 51. Solid state IR spectrum of $Mo_2O_4(OH)_4((NMe_2)PheH)$

Oxomolybdate backbone

Several recurring oxo species are found in high valent molybdenum complexes.[3] These have one or more oxygen atoms as terminal or bridging ligands and are generally indicated as $[Mo_xO_y]^{n+}$ (see section 1.3). Both stretching and deformation vibrations of molybdenum-oxygen bonds give rise to strong and characteristic bands in the IR and Raman spectra and thus vibrational spectroscopy is a valuable method for the determination of the structure of such species.[228] The IR features of terminals and bridging oxo ligands are outlined below, followed by the ensuing considerations about the IR spectra of complexes **1-6**.

IR features of terminal molybenum-oxygen bonds - A complex with the $[MoO]^{4+}$ group has only one infrared mode due to the molybdenum-oxygen stretching vibration. For a *cis*-dioxo group, $[MoO_2]^{2+}$, three infrared and Raman active modes are expected: a symmetric stretching, $v_s(MoO_2)$, an antisymmetric stretching, $v_s(MoO_2)$, and a deformation vibration, $\delta(MoO_2)$.[38,228] Four modes are expected for the $[MoO_3]$ group (C_{3v} symmetry), all infrared and Raman active: two stretching vibrations, $v_s(MoO_3)$ and $v_a(MoO_3)$, and two deformation vibrations, $\delta_s(MoO_3)$ and $\delta_a(MoO_3)$. Table 21 reports the vibrational frequencies for some structurally-determined mononuclear or non-oxo bridged polynuclear molybdenum(VI) compounds with one, two, three or four terminal oxo ligands.

Tab. 21. Infared vibrations of terminal [MoO$_x$] groups in some structurally-determined molybdenum(VI) complexes

[MoO$_x$] Group	Compound	IR Bands (cm^{-1}) with vibrational assignments			Notes*	Ref.

		ν(MoO)				
	[CpMoOCl$_2$]	949				[229]
	MoOCl$_4$	997			square pyramidal	[230]
	MoOF$_4$	about 1100			actually MoOF$_3$(μ-F)$_2$	[54]
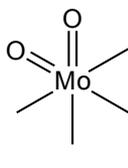
		ν_s(MoO$_2$)	ν_a(MoO$_2$)	δ(MoO$_2$)		
	Na$_2$[MoO$_2$F$_4$]·H$_2$O	951	920	385	Raman	[38]
	K$_2$[MoO$_2$F$_4$]·H$_2$O	960	917	403		[38]
	(NH$_4$)$_3$[MoO$_2$F$_5$]	953	887	410		[38]
	K$_3$[Mo$_2$O$_4$F$_7$]	967 and 953	919 and 900	374	actually μ-F polymer	[38]
	(NH$_4$)$_5$[Mo$_3$O$_6$F$_{11}$]·H$_2$O	959	894	374	actually μ-F polymer	[38]
	Cs$_2$[MoO$_2$Cl$_4$]	919	883	381		[228,231]
	[K(18-crown-6)][MoO$_2$Cl$_3$(H$_2$O)]	957 and 944	894	251	KBr disk	[232]
	[MoO$_2$Cl$_2$(MeOH)$_2$]·18-crown-6	957 and 951	909	260	KBr disk	[232]
	[CpMoO$_2$Cl]	920	877	397		[229]
	[MoO$_2$Cl$_2$(DMF)$_2$]	939	905	*n.r.*		[233]
	[MoO$_2$Cl$_2$(H$_2$O)$_2$]	957 and 951	909	260	KBr disk	[232]
	[MoO$_2$Br$_2$(bipy-κN,$\kappa N'$)]	934	903	*n.r.*		[234]
	[MoO$_2$Br$_2$(H$_2$O)$_2$]	957 and 948	907	248	KBr disk	[232]
	[MoO$_2$(C$_9$H$_6$NO-κN,κO)$_2$]	926	899	*n.r.*	*8-hydroxyquinolinate*	[235-237]
	[MoO$_2$(acac-κO,$\kappa O'$)$_2$]	935	904	*n.r.*		[237-239]
	[MoO$_2$(MeCOCHCOPh-κO,$\kappa O'$)$_2$]	939	909	*n.r.*	KBr disk	[237]
	[MoO$_2$(C$_{15}$H$_{11}$O$_2$-κO,$\kappa O'$)$_2$]	931	899	*n.r.*	*1,3-Diphenylpropane-1,3-dione*	[237,240]
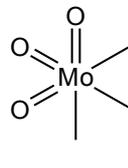
		ν_s(MoO$_3$)	ν_a(MoO$_3$)	δ_s(MoO$_3$) δ_a(MoO$_3$)		
	[MoO$_3$(dien-κN,$\kappa N'$-$\kappa N''$)]	839	826	380 (*deg.*)		[38,39]
	Na$_4$[Mo$_2$O$_6$(EDTA)]	892	815	374 / 340	IR (Nujol) + Raman bridging EDTA ligand	[70,228,241]
	(NH$_4$)$_3$[MoO$_3$F$_3$]	900	813	371 / 360		[38]
	K$_3$[MoO$_3$F$_3$]	911	872 and 840	363 (*deg.*)		[38]
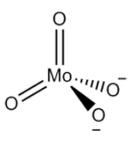
		The two higher-frequency modes for a ML$_4$ tetrahedral species				
	Na$_2$[MoO$_4$]·2H$_2$O	899 ; 854 ; 815 ; 805			ATR	[242]
	(NH$_4$)$_2$[MoO$_4$]	887 ; 870 ; 853 ; 839			ATR	[242]

* Spectra were recorded as Nujol, HCBD or other mull except where noted. When necessary, ligands are indicated in italics. Deg. = degenerate deformation bands

Wavenumbers for stretching modes are found in the 800-1000 cm^{-1} range, while the corresponding deformation modes are found in the far-infrared region (300-400 cm^{-1}). The actual value depends on the nature of the oxo species, the oxidation state of molybdenum and the ligands.[3]

Due to the multiple nature of terminal molybdenum-oxygen bonds, their vibrational frequencies are sensitive to changes in the degree of metal-oxygen π-bonding.[228] As table 21 shows, Mo−O stretching wavenumbers decrease in the order $[MoO]^{4+}$ > $[MoO_2]^{2+}$ > $[MoO_3]$ ≈ $[MoO_4]^{2-}$. This trends correlates with the expected decrease in π-bonding in these molybdenum(VI) complexes.[3] For example, the stretching vibration for a $[MoO]^{4+}$ group, the highest in this series, is observed around 950-1000 cm^{-1}. This frequency range agrees with that usually observed for monooxo complexes of other early transition metals, indicating the presence of two strong metal-oxygen π bonds.[243] At the opposite extreme, for octahedral MoO_3 species and for the tetrahedral $[MoO_4]^{2-}$ anion, the higher absorption is observed around 900 cm^{-1} and a Mo−O bond order of 2.0 has been calculated.[39]

In conclusion, the number of terminal molybdenum-oxygen bonds can easily be identified on the basis of wavenumbers of stretching absorptions. Instead, the comparison between the number of bands observed and expected vibrational modes is not reliable, since solid state effects of and / or overlapping bands may play a role.

IR features of bridging molybenum-oxygen bonds - Polynuclear molybdenum(VI) complexes with one or two bridging oxo ligands show additional bands in the 700-900 cm^{-1} region and these, when they can be distinguished from other ligand vibrations, have been assigned to bridge vibrations.[3] A single bridging oxygen (Mo−O−Mo or *Mo₂O*) is characterized by a symmetric stretching, $v_s(Mo_2O)$, an antisymmetric stretching, $v_a(Mo_2O)$, and a bending vibration, $\delta(Mo_2O)$.[228] In the case of a bent bridge, all three modes are Raman and IR active, while the symmetric stretching for a linear Mo−O−Mo bridge is only Raman active if the complex is centrosymmetrical.[244] The bending vibrations of monobridged complexes fall in the far infrared region (200-300 cm^{-1})[228] and are often not reported.

Two stretching modes are also associated with the double oxo bridge: a symmetric vibration, $v_s(Mo_2O_2)$, which is IR inactive for a centrosymmetrical structure, and an antisymmetric vibration, $v_a(Mo_2O_2)$.[228] The third, lower-energy vibration is associated to a bending mode.[245]

Table 22 reports the vibrational frequencies for some structurally-determined polynuclear oxomolybdenum compounds with different $[Mo_xO_y]$ bridging groups.

Tab. 22. Infared vibrations of bridging [Mo$_x$O$_y$] groups in some structurally-determined molybdenum(VI) complexes

[Mo$_x$O$_y$] Group	Compound	IR Bands (cm^{-1}) with vibrational assignments		Notes*	Ref.
180° Mo—O—Mo		ν_a(Mo$_2$O)			
	[(CpMoO$_2$)$_2$(μ-O)]	770			[229,246]
	(NH$_4$)$_2$[MoO$_3$F$_2$]	820		actually {MoO$_2$F$_2$(μ-O)}$_n^{2n-}$	[38]
	[((^{t}Bu$_3$tacn)MoO$_2$)$_2$(μ-O)](OTf)$_2$	782		KBr disk *Bu$^t_3$tacn = 1,4,7-tributyl-1,4,7-triazacyclonane*	[247]
Mo—O—Mo		ν_a(Mo$_2$O)	ν_s(Mo$_2$O)		
	K$_2$[MoO$_3$(C$_2$O$_4$)]	744	*n.r.*	KBr disk actually {MoO$_2$(μ-O)(C$_2$O$_4$)}$_n^{2n-}$	[248]
	(NH$_4$)$_2$[MoO$_3$(μ-O)MoO$_3$]	682	476	KBr disk	[249]
	NH$_4$(enH$_2$)$_{0.5}$[Co(en)$_3$][Mo$_2$O$_7$(C$_2$O$_4$)]·H$_2$O	759	*n.r.*	KBr disk	[250]
	[Mo$_2$O$_4$(μ-O)Cl$_2$(PzPy)$_2$]·3CH$_3$CN	773	448	ATR	[251]
Mo—O—Mo (with bridging O below)		ν_a(Mo$_2$O$_2$)	ν_s(Mo$_2$O$_2$)		
	[MoO(μ-O)(C$_6$H$_4$(2-O)CH=N^1-N^2=C(S)N^{3}H$_2$-κO,κN^1,κS)]$_2$	840	767	KBr disk asymmetric	[252]
	(Et$_2$NHOH)$_2$[Mo$_2$O$_4$(Et$_2$NO)$_2$(C$_2$O$_4$)$_2$]	582	IR inactive	centrosymmetric	[253]
	[Et$_4$N]$_2$[Mo$_2$O$_4$(μ-O)$_2$(Pic-κN,κO)$_2$]	a number of features around 700-860 cm^{-1}			[74]
	H$_2$[Mo$_2$O$_4$(SCH$_2$CH$_2$N(CH$_3$)(CH$_2$)$_3$N(CH$_3$)CH$_2$CH$_2$S-κS,κS')$_2$]	740	*n.r.*	KBr disk	[254]
	[MoO(μ-O)(C$_6$H$_4$(2-O)CH=NCH$_2$CH$_2$O-κN,κO,κO')]$_2$	840 ; 830	760	asymmetric	[255]
	[MoO(μ-O)(X$_2$NCH$_3$-κN,κO,κO')]$_2$ X = C$_6$H$_2$(5-Me)(3-Me/^{t}Bu)(2-O)CH$_2$	822-818	766-760	asymmetric	[256]
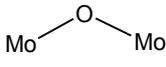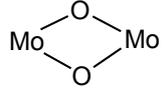
* Spectra were recorded as Nujol, HCBD or other mull except where noted. When necessary, ligands are indicated in italics. For Mo$_2$O$_2$ complexes, the geometry is specified (asymmetric or centrosymmetric)

As evident from table 22, the distinction between absorptions due to different bridging oxo groups is a difficult task. However, it is possible to make some useful considerations.

The only IR active stretching vibration for compounds with a linear Mo$_2$O bridge generally falls in the 750-800 cm^{-1} range[245] while the antisymmetric stretching band for a bent Mo$_2$O bridge was generally found around 720-760 cm^{-1}, with a medium to strong intensity.[38]

For a M−O−M bent bridge (M is a transition metal), ν_a(M$_2$O) is expected to be found at a wavenumber at least 215 cm^{-1} higher than ν_s(M$_2$O).[245] This observation also applies to Mo(VI) complexes (see table 22), for which a medium to strong band in the 430-480 cm^{-1} region may be assigned to the symmetrical Mo−O−Mo bridge stretching.

The Mo$_2$(μ-O)$_2$ ring is very common for Mo(V) complexes, in which is often supported by a metal-metal bond.[257] These compounds, if not centrosymmetric, show three bands attributable to bridge modes: two stretching modes around 700-750 cm^{-1} and a third vibration about 100 cm^{-1} lower in wavenumber.[245] Instead, the asymmetric Mo$_2$(μ-O)$_2$ ring is often found in Mo(VI) complexes with only one terminal oxo ligand for each molybdenum.[258] These compounds show two strong bands around 830 and 760 cm^{-1} associated respectively to ν_a(Mo$_2$O$_2$) e ν_s(Mo$_2$O$_2$).

Molybdenum(VI) compounds with a symmetric double bridge show the ν_a(Mo$_2$O$_2$) band in a more extended range and at lower frequencies (see table 22).

Remarks on IR spectra of Mo$_2$O$_4$(OH)$_4$(aaH) complexes - IR spectra of complexes **1-6** show three strong absorptions around 944, 915 and 902 cm^{-1}. The wavenumbers of these bands indicates the presence of a *cis*-MoO$_2$ group. The splitting of the antisymmetric stretching band may be due to a solid-state effect, as already observed in some compounds (see table 20), or to the fact that the two MoO$_2$ groups are different in a dinuclear complex.[p] The medium intensity band around 760 cm^{-1} can be assigned to the asymmetric stretching of a bent Mo−O−Mo bridge and / or a Mo$_2$O$_2$ double bridge. The corresponding ν_s(Mo$_2$O$_2$) could be hidden in the broad absorption around 500 cm^{-1} while the absorption around 470 cm^{-1} is assigned to ν_s(Mo$_2$O). This suggest that the Mo−O frame of our compounds can be one of the three represented in figure 52.
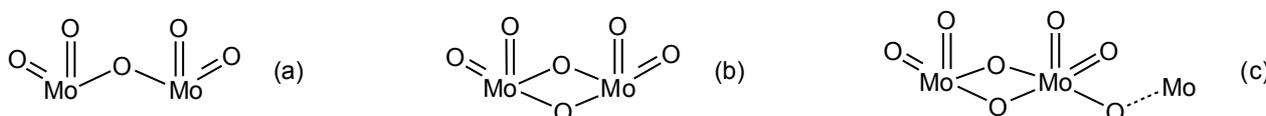
Fig. 52. The *cis*-MoO$_2$ groups in complexes **1-6** are likely to have a bent oxo bridge (a), a double oxo bridge (b) or both (c)

The carboxylate group

Several binding modes of a carboxylate (RCO$_2{}^-$) to a metal centre have been characterized. Apart from ionic compounds, the most common coordination forms are monodentate, M(OC(O)R-κO), bidentate chelating, M(O$_2$CR-κO,$\kappa O'$) and bidentate bridging, M$_2$(μ-O$_2$CR-κO,$\kappa O'$).[259] These are depicted in figure 53.
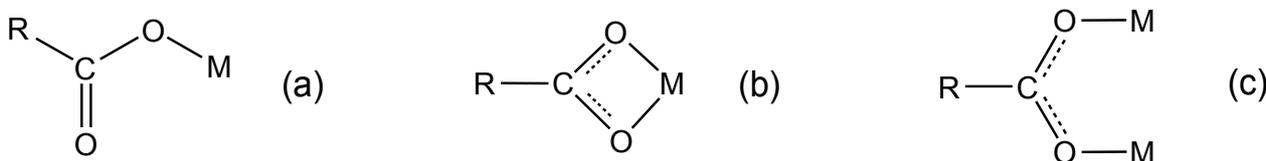
Fig. 53. Monodentate (a), bidentate chelating (b) and bidentate bridging (c) coordination modes of a carboxylate ligand

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p   It is interesting to note that absorptions at 940, 926 and 891 cm^{-1} are reported also for the *cis*-MoO$_2$ group in K$_2$[HMo$_6$VO$_{22}$(NH$_3$CH$_2$COO)$_3$],[101] which contains three (MoO$_2$)$_2$(μ-O)$_2$ units, each one with a bidentate bridging glycine ligand (see section 1.4)

IR spectroscopy proved to be an useful tool for distinguishing between monodentate, chelating and bridging coordination modes of a carboxylate ligand. A carboxylate group has two well-known IR active vibrational modes: the symmetric stretching, $\nu_s(CO_2^-)$, and the antisymmetric stretching, $\nu_a(CO_2^-)$. These stretching modes give rise to strong absorptions around 1400 and 1600 cm^{-1} respectively, in both solid state and in solution. The wavenumber separation between the two bands, (22), has been investigated in several studies as a correlation parameter between the carboxylate coordination and its stretching frequencies.[260-262]

$$\Delta\nu_{a-s} = \nu_a\left(CO_2^-\right) - \nu_s\left(CO_2^-\right) \tag{22}$$

Deacon and Philips[261] carefully examined the solid state IR spectra of many acetate and trifluoroacetate complexes with known crystal structures and compared $\Delta\nu_{a-s}$ values with the ones for the respective sodium or potassium salts. Their conclusions are summarized below:

- Values of $\Delta\nu_{a-s}$ that are markedly greater than $\Delta\nu_{a-s}$ in the ionic compounds are indicative of a monodentate carboxylate coordination (type (a) in figure 53)

- Values of $\Delta\nu_{a-s}$ that are significantly lower than $\Delta\nu_{a-s}$ in the ionic compounds are indicative of a bidentate chelating coordination (type (b) in figure 53). For acetates only, it has been observed this case also for complexes in which the ligand bridges two metals linked by a short metal-metal bond

- Values of $\Delta\nu_{a-s}$ for bridging complexes are greater than those of chelating complexes and close to the ionic value (type (c) in figure 53)

The theoretical background of such correlation between the vibrational frequencies of a carboxylate and its coordination has been proposed by Tasumi et al.[263] Through *ab initio* MO calculations, they showed that the $\Delta\nu_{a-s}$ value in metal acetates is linearly related to changes in C–O bond lengths and in the O–C–O angle. There is a considerable reduction of symmetry in C–O bond distances when moving from the free ion to a monodentate coordination. As a consequence, the two C–O bonds vibrate almost independently and the two frequencies diverge, causing the value of $\Delta\nu_{a-s}$ to increase. In a chelating coordination, the C–O bond distances are almost identical, although longer than the in free ion, while the O–C–O angle is reduced significantly. This has been related to the convergence of the two vibration frequencies and thus explains why the value of $\Delta\nu_{a-s}$ diminishes substantially. The symmetry of a carboxylate in a bridging coordination, especially if the two metals are identical, is not much different from that of the free carboxylate. For this reason, the corresponding $\Delta\nu_{a-s}$ values are expected to be not too different from the ionic value. These effects markedly decrease in the order $Mg^{2+} > Ca^{2+} > Na^+$

following the increase in ionic character of the bond.

It is important to note that the two discriminatory values, as well as the ionic reference value, depend on the particular molecule. For acetate complexes ($\Delta\nu_{a-s}$ = 164 cm^{-1} for CH$_3$COONa[264]), a value of $\Delta\nu_{a-s}$ > 200 cm^{-1} is indicative of monodentate coordination, while a value of $\Delta\nu_{a-s}$ < 150 cm^{-1} is indicative of bidentate chelating coordination. Sodium trifluoroacetate has $\Delta\nu_{a-s}$ = 223 cm^{-1} and $\Delta\nu_{a-s}$ > 260 cm^{-1} is considered significantly higher, while $\Delta\nu_{a-s}$ < 200 cm^{-1} is considered significantly lower.[261] Moreover, the nature and oxidation state of the metal may exert a significant influence on the interval in which $\Delta\nu_{a-s}$ varies.

For these reasons, carboxylate stretching vibrations of structurally determined molybdenum(VI) complexes have been compared with $\Delta\nu_{a-s}$ values for the corresponding sodium carboxylates. Since α-amino acids are zwitterionic in the solid state, they may represent a good ionic reference as well. Results are summarized in table 23, 24 and 25 for a monodentate, chelating and bridging coordination, respectively.

Tab. 23. IR comparison between structurally determined oxomolybdenum(VI) complexes with monodentate carboxylate ligands and corresponding ionic references (in italics)

Carboxylic acid	Compound*	$\nu_a(CO_2^-)$ /cm^{-1}	$\nu_s(CO_2^-)$ /cm^{-1}	$\Delta\nu_{a-s}$ (CO_2^-)/cm^{-1}	Ref.
Glycolic Acid HOCH$_2$COOH	*HOCH$_2$COONa*	*1598*	*1438*	*160*	[186]
	K$_2$[MoO$_2$(**O**CH$_2$CO**O**)$_2$]·H$_2$O	1666	1392	274 (*+114*)	[265]
	[PPh$_4$][MoO$_2$(**O**CH$_2$CO**O**)(**O**CH$_2$COOH)]	1627	1328	299 (*+139*)	[266]
Lactic Acid CH$_3$CH(OH)COOH	*CH$_3$CH(OH)COONa*	*1590*	*1421*	*169*	[186]
	Na$_2$[MoO$_2$(**O**CH(CH$_3$)CO**O**)$_2$]·H$_2$O	1650	*1390*	260 (*+91*)	[265]
Alanine CH$_3$CH(NH$_2$)COOH	*DL-CH$_3$CH(NH$_3^+$)COO$^-$*	*1594*	*1410*	*184*	[186]
	Na$_4$[Mo$_8$O$_{26}$(CH$_3$CH(NH$_3$)CO**O**)$_2$]·18H$_2$O	1659	1398	261 (*+77*)	[100,267]
Proline (NH(CH$_2$)$_3$)CHCOOH	*DL-NH$_3^+$(CH$_2$)$_3$CHCOO$^-$*	*1611*	*1416*	*195*	[186]
	Na$_4$[Mo$_8$O$_{26}$(**O**COCH(CH$_2$)$_3$NH$_2$)]·22H$_2$O	1632	1384	248 (*+53*)	[268]
Mandelic Acid PhCH(OH)COOH	*DL-PhCH(OH)COONa*	*1607* *1625*	*1428* *1411*	*196 (avg)*	[186]
	(NH$_4$)$_2$[MoO$_2$(PhCH(**O**)CO**O**)$_2$]·8H$_2$O	1635	1364	271 (*+75*)	[269]
Salicylic Acid C$_6$H$_4$(*p*-OH)COOH	*C$_6$H$_4$(p-OH)COOLi*	*1571*	*1414*	*157*	[186]
	[NMe$_4$]$_2$[MoO$_2$(C$_6$H$_4$(p-**O**)COO)$_2$]	1598	1359	239 (*+82*)	[270]
Glycylglycine H$_2$NCHCONHCH$_2$COOH	*$^+$H$_3$NCHCONHCH$_2$COO$^-$*	*1600*	*1409*	*191*	[271]
	Na$_4$[Mo$_8$O$_{26}$(H$_3$NCHCONHCH$_2$CO**O**)$_2$]·15H$_2$O	1636	1382	254 (*+63*)	[267]

* Donor atoms are marked in bold

Tab. 24. IR comparison between structurally determined oxomolybdenum(VI) complexes with bidentate chelating carboxylate ligands and corresponding ionic references (in italics)

Carboxylic acid	Compound*	$\nu_a(CO_2^-)/$ cm^{-1}	$\nu_s(CO_2^-)$ /cm^{-1}	$\Delta\nu_{a-s}(CO_2^-)$/cm^{-1}	Ref.
Acetic Acid CH_3COOH	*CH_3COONa*	*1563*	*1413*	*150*	[186]
	$\{K[MoO_2(\mathbf{O}COCH_3)_2(\mathbf{O}COCH_3)]\cdot CH_3COOH\}_n$	1560	1444	116 (*−34*)	[272]
Salicylic Acid $C_6H_4(p\text{-}OH)COOH$	*$C_6H_4(p\text{-}OH)COOLi$*	*1571*	*1414*	*157*	[186]
	$[PPh_4][MoO(O_2)_2(C_6H_4(p\text{-}OH)C\mathbf{OO})]$	1585	1481	104 (*−53*)	[169]
Benzoic Acid C_6H_5COOH	*C_6H_5COONa*	*1553*	*1413*	*140*	[186]
	$[PPh_4][MoO(O_2)_2(C_6H_5C\mathbf{OO})]$	1580	1500	80 (*−60*)	[273]

* Donor atoms are marked in bold

Tab. 25. IR comparison between structurally determined oxomolybdenum(VI) complexes with bidentate bridging carboxylate ligands and corresponding ionic references (in italics)

Carboxylic acid	Compound*	$\nu_a(CO_2^-)$ /cm^{-1}	$\nu_s(CO_2^-)$ /cm^{-1}	$\Delta\nu_{a-s}(CO_2^-)$/cm^{-1}	Ref.
	$^+H_3NCH_2COO^-$	*1610*	*1412*	*211*	[223]
	$K_2[HMo_6VO_{22}(H_3NCH_2C\mathbf{OO})]\cdot 8H_2O$	1612	1420	192 (*−19*)	[101]
	$K_2[Mo_6SeO_{21}(H_3NCH_2C\mathbf{OO})]\cdot 8H_2O$	1605	1422	183 (*−28*)	[102]
Glycine H_2NCH_2COOH	$K_2[Mo_6(POH)O_{21}(H_3NCH_2C\mathbf{OO})]\cdot 8.5H_2O$	1610	1422	188 (*−23*)	[103]
	$K_2[Mo_6(PCH_3)O_{21}(H_3NCH_2C\mathbf{OO})]\cdot 8.5H_2O$	1607	1423	184 (*−27*)	[103]
	$K_2[Mo_6(PH)O_{21}(H_3NCH_2C\mathbf{OO})]\cdot 8H_2O$	1614	1416	198 (*−13*)	[103]
Pyridine-3-carboxylic acid $C_5H_4N(3\text{-}COOH)$	*$C_5H_5N(3\text{-}COONa)$*	*1603*	*1407*	*196*	[186]
	$\{Mo_2O_6(C_5H_5NC\mathbf{OO})\}_n$	1637	1416	221 (*+25*)	[274]
β-alanine $H_2NCH_2CH_2COOH$	*$^+H_3NCH_2CH_2COO^-$*	*1579*	*1413*	*166*	[186]
	$K(H_3NCH_2CH_2COOH)[Mo_6TeO_{21}(H_3NCH_2CH_2C\mathbf{OO})]\cdot 3H_2O$	1626	1417	209 (*+40*)	[102]
Alanine $CH_3CH(NH_2)COOH$	*$L\text{-}CH_3CH(NH_3^+)COO^-$*	*1589*	*1413*	*176*	[186]
	$K_2[Mo_6TeO_{21}(CH_3CH(NH_3)C\mathbf{OO})]\cdot 4.5H_2O$	1605	1422	183 (*+7*)	[102]
4-Amino-*n*-Butyric Acid $H_2N(CH_2)_3COOH$	*$^+H_3N(CH_2)_3COO^-$*	*1599*	*1402*	*197*	[186]
	$Cs_2[Mo_6TeO_{21}(CH_3CH(NH_3)C\mathbf{OO})]\cdot 5.25H_2O$	1622	1423	199 (*+2*)	[102]

* Donor atoms are marked in bold

Data in table 23-25 show a good correlation between the value of $\Delta\nu_{a-s}$ and the coordination mode of the carboxylate ligand in dioxomolybdenum(VI) complexes. Compounds with monodentate carboxylate ligands show values of $\Delta\nu_{a-s}$ greater than about 80 cm^{-1} with respect to the ionic reference, while $\Delta\nu_{a-s}$ is less than about 50 cm^{-1} for compounds with carboxylate chelating ligands. Compounds having a bidentate bridging ligand, show values of $\Delta\nu_{a-s}$ close to the ionic reference value (± 20 cm^{-1} on average).

As shown in table 20, $Mo_2O_4(OH)_4(aaH)$ complexes have $\Delta\nu_{a-s}$ values that are ± 20 cm^{-1} on average with respect to their ionic reference (the zwitterionic amino acid in the solid state). These shifts, for a Mo(VI) compound, are not large enough for a monodentate coordination nor too small for a chelating coordination. This supports the idea of a bridging coordination of the carboxylate moiety (see figure 54).
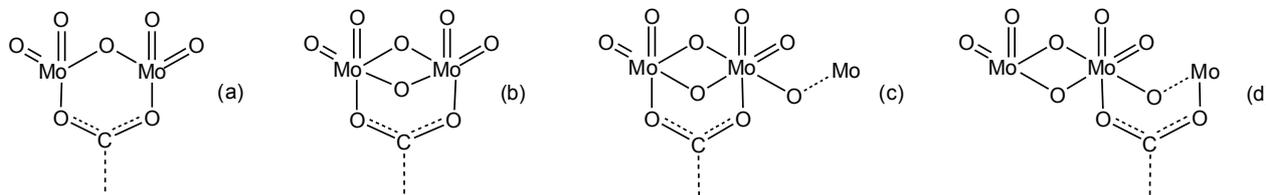
Fig. 54. The four possible structures (a-d) obtained by adding a carboxylate bridging ligand to the three structures shown in figure 52

IR bands of the ammonium group and other considerations

The C–H and N–H stretching vibrations of organic compounds are typically found in the 2800-3300 cm^{-1} region of the IR spectrum.[275] N-Bonded amino acid complexes of the first transition elements show rather sharp bands due to N–H stretchings in a higher frequency region than those of the free ligand.[219,259,276,277] Conversely, the N–H stretching bands of molybdenum(VI) complexes **1-6** are weak and broad. It is interesting to note that there is a striking similarity in the 2800-3300 cm^{-1} region of the IR spectrum between $Mo_2O_4(OH)_4(aaH)$ and the corresponding ammonium acid nitrate, $[aaH_2]NO_3$. Figure 55 show this comparison for glycine, L-phenylalanine, L-leucine and L-methionine.

In the 1400-1600 cm^{-1} region of $Mo_2O_4(OH)_4(aaH)$ spectra (aaH = GlyH, PheH, LeuH, MetH), the antisymmetric $\delta_a(NH_3^+)$ and symmetric $\delta_s(NH_3^+)$ deformation bands of the ammonium group are recognizable.[278] In the L-proline complex, there is only one deformation band, as expected for a secondary ammonium ion.[279] These absorptions are only slightly shifted with respect to the free amino acid.

Regarding the (NMe_2)PheH complex, no bending is observed since this mode is not expected for a tertiary ammonium ion.[278] However it may be noted that substantially no shift is observed for the stretching vibration of the N–CH$_3$ bond, which falls around 1490 cm^{-1} both in the complex and in the free amino acid.[280]

These observations clearly indicate that the amino group in these complexes is protonated (see figure 56).[q] This is reasonable, keeping in mind that the pH of the reaction mixture was around 2, a value much lower than the isoelectric point of the amino acids used (pI $\approx$ 6).[78]

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q   The interpretation of ^{13}C CP-MAS isotropic chemical shifts supports the zwitterionic nature of the amino acid ligand, see section 3.3
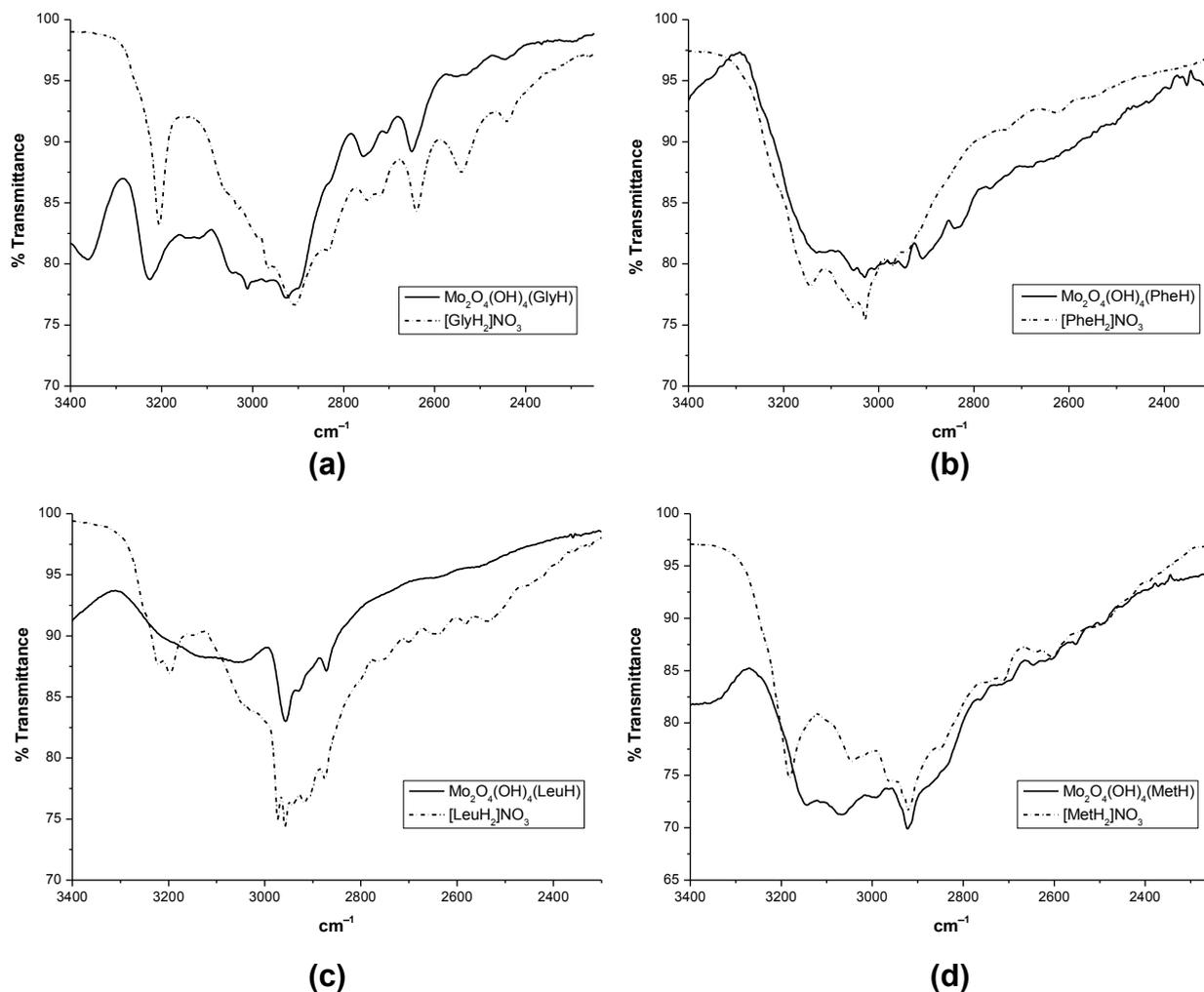
Fig. 55. Comparison of Mo$_2$O$_4$(OH)$_4$(aaH) (straight line) and [aaH$_2$]NO$_3$ (dashed line) IR spectra in the 2300-3400 cm^{-1} interval for glycine (a), L-phenylalanine (b), L-leucine (c) and L-methionine (d)
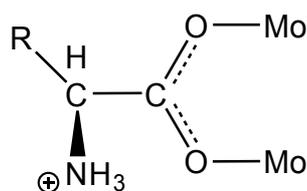
Fig. 56. A generic zwitterionic α-amino acid with its carboxylate group involved in a bidentate bridging coordination with two molybdenum atoms

The deformation of the −SCH$_3$ group is another characteristic and intense band[281] which falls at 1316 cm^{-1} in the spectrum of L-methionine and at 1334 cm^{-1} in the spectrum of Mo$_2$O$_4$(OH)$_4$(MetH). A medium intensity absorption at 1333 cm^{-1} was found in the IR spectrum of two structurally determined L-methionine complexes of Nb(V) and Ta(V) in which the ligand is bonded through the amino and the carboxylate groups.[282] This suggests that the sulphur atom in Mo$_2$O$_4$(OH)$_4$(MetH) is not involved in coordination with molybdenum.
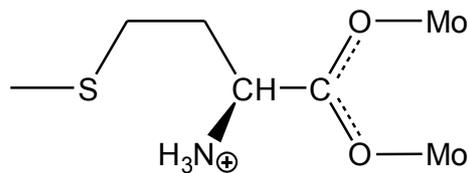
Fig. 57. The proposed coordination for L-methionine in complex **4**

Complexes **1-6** also show a broad absorption around 3400-3600 cm^{-1}. This range is typical for the O–H stretching vibration[259] and may be due hydroxo or water ligands, which are necessary to complete the coordination of molybdenum atoms.

Formation of Mo–O bonds with organic ligands results in the appearance of a few medium to strong stretching absorptions in the 550-650 cm^{-1} region.[38,253,283] All the Mo$_2$O$_4$(OH)$_4$(aaH) complexes display a strong and broad band in this wavenumber interval. The remarkable width of this band may indicate the presence of different Mo–O$_{ligand}$ bonds. The aforementioned ν_s(Mo$_2$O$_2$) band may also contribute.

Section 3.5 - DFT calculations

Synthesis conditions, elemental analysis, IR and NMR characterization led to the following firm points about the structure of the synthesized complexes:

- Molybdenum is bonded to two terminal oxygens, forming a *cis*-MoO$_2$ group. A Mo−O−Mo bent bridge and / or a Mo$_2$O$_2$ double bridge are also present

- The zwitterionic amino acid ligand is involved in a bidentate bridging coordination through its carboxylate group

- These complexes are neutral and contain 2 molybdenum atoms for each amino acid ligand. The elemental composition is consistent with the formula (MoO$_3$)$_2$(aaH)(H$_2$O)$_2$

Thus, oxo, hydroxo and / or water ligands need to be added to complete the coordination sphere. Many possible structures fulfil the requirements of electroneutrality and hexacoordination of molybdenum.[r] DFT calculations helped to discriminate among them.

First, the attention was focused on non-chained structures. The three structures hypothesized, excluding geometrical isomers and non-symmetrical disposition of ligands, are reported in figure 58 (**a**−**c**). A fourth structure (**d**) with pentacoordinated molybdenum atoms is also reported. This structure was proposed by Castillo et al.,[136] during their investigation of molybdenum(VI)-amino acid complexes (see section 1.5).
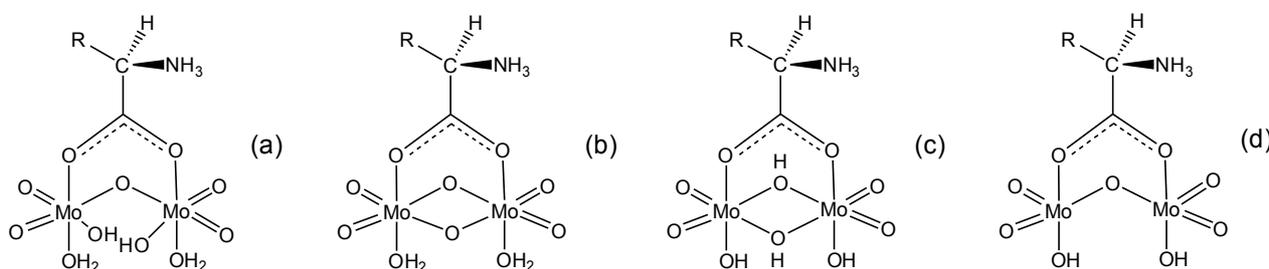
Fig. 58. Non-chained structures initially hypothesized for Mo$_2$O$_4$(OH)$_4$(aaH)[s]

Structures **a**−**d**, with R = H (Glycine), were subjected to DFT gas-phase optimization performed by Dr. M. Bortoluzzi of the Università Cà Foscari (Venezia).

Ten optimized structures were obtained in total.[t] The optimization of structure **d** led to two minimum structures with a very low stability (< −10 kcal·mol^{-1}). This result is consistent with the preference of molybdenum for the hexacoordination.[r]

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r   The predominance of hexacoordination for Molybdenum(VI) oxo complexes has been discussed in section 1.3.

s   Structures **b** and **c** correspond exactly to the formula (MoO$_3$)$_2$(aaH)(H$_2$O)$_2$ while structure **a** corresponds to (MoO$_3$)$_2$(aaH)(H$_2$O)$_3$ and structure **d** corresponds to (MoO$_3$)$_2$(aaH)(H$_2$O)

t   Their stability is discussed in relative terms, with respect to the least stable structure, to which an energy of 0 is assigned. The energy data are related to electronic energy states corrected for the electrostatic nuclear potential.

The optimization of **a** and **b** led to three structures in total, characterized by a low stability (two < −18 kcal·mol^{-1} and one is the least stable) and a displacement of ligands that is strongly divergent from the one initially proposed. It is interesting to note that water molecules are either completely dissociated or only weakly bonded to molybdenum. This observation tends to rule out the presence of water as a ligand. Moreover, a second bridge with an hydroxy ligand was present in the optimized structure of **a**. This supports the idea of a doubly bridged structure (triply bridged if the amino acid is also considered).

The optimization of **c** led to five minimum structures of a good stability, differing only in geometry from the original structure. The two most stable structures, named *Gly-I* and *Gly-II*, are shown in figure 59. Selected bond distances and angles are reported in table 26.
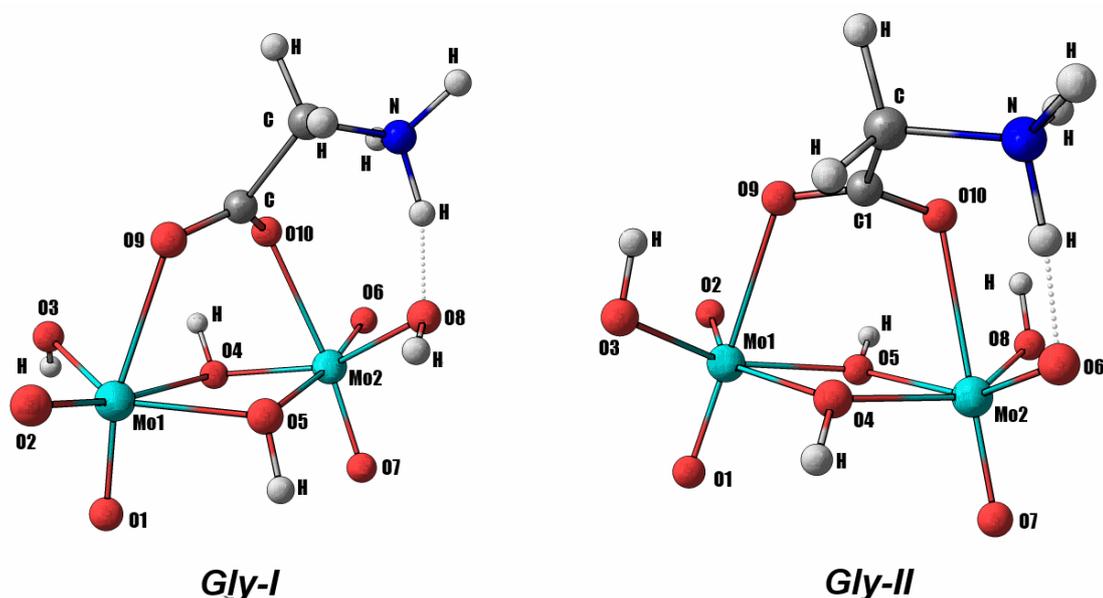
Fig. 59. Most stable optimized structures for the Mo$_2$O$_4$(OH)$_4$(GlyH) structure hypothesis

Structures *Gly-I* (−23.8 kcal·mol^{-1}) and *Gly-II* (−27.3 kcal·mol^{-1}) are built up of dinuclear molecules [(MoO$_2$(OH))$_2$(μ-OH)$_2$(μ-O$_2$CCH$_2$NH$_3$-κO,κO')]. Each molybdenum atom is bonded to two terminal oxygen atoms (average Mo−O bond length = 1.70 Å, significantly shorter than the others Mo−O bond lengths) and one hydroxo ligand (average Mo−O bond length = 1.90 Å). The two MoO$_2$(OH) units are bridged by two hydroxo ligands and the carboxylate group of glycine. One bridging OH ligand and one carboxylic oxygen are *trans* to a terminal oxo ligand. The three angles between molybdenum and terminal ligands are greater than 90 ° (ca. 105 °) while O−Mo−O angles with bridging ligands are lower than 90 ° (70-80 °): this leads to a distorted octahedral coordination.

Each bridging oxygen atom is more closely associated with a single molybdenum, giving

rise to an asymmetric $Mo_2(OH)_2$ ring.[u] Structure *Gly-I* is also characterized by a slightly asymmetric coordination of glycine (Mo(1)−O(9) = 2.418 Å; Mo(2)−O(10) = 2.346 Å). The asymmetry of both bridging OH ligands and the carboxylate coordination is well reduced in *Gly-II*. The two structures differ also in the position of the intermolecular hydrogen bond, that involves a proton of the −NH₃ group and a terminal −OH ligand in *Gly-I* while a terminal oxo group in *Gly-II*.

Since the experimental behaviour of the six different amino acids used was very similar, it may be expected that the molybdenum-oxygen backbone is not significantly influenced if changing the amino acid side-chain.

As a confirmation, two optimized structures were found for the *N,N*-dimethyl-L-phenylalanine complex, which are very similar to those found for glycine. Figure 60 reports the most stable optimized structure (of about 4 kcal·mol⁻¹), named *dmPhe-I* (selected bond distances and angles are reported in table 26). The only substantial difference between the optimized structures with glycine and the ones with *N,N*-dimethyl-phenylalanine is that both *dmPhe-I* and *dmPhe-II* (not shown) have no hydrogen bond, despite that the ammonium group has an available proton. This suggests that the presence of intermolecular hydrogen bonds involving the ammonium group of the α-amino acid is not crucial for the stability of this type of structures.
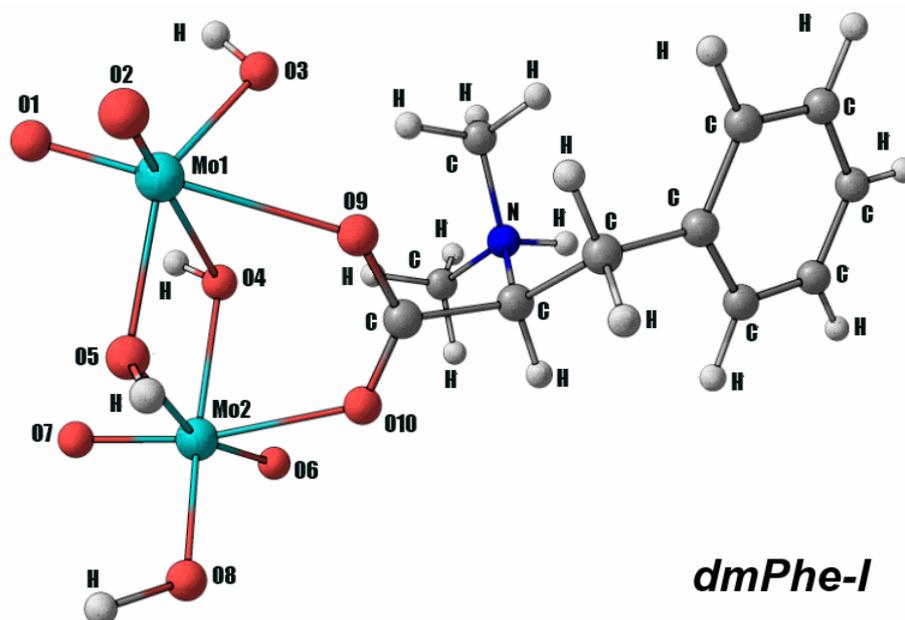
Fig. 60. Most stable optimized structure for the $Mo_2O_4(OH)_4((NMe_2)PheH)$ structure hypothesis

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u   For example, in *Gly-I* there are two longer bonds (Mo(1)−O(4) = 2.363 Å and Mo(2)−O(5) = 2.573 Å) when the bridging OH is trans to a terminal oxo ligand and two shorter bonds (Mo(1)−O(5) = 2.076 Å and Mo(2)−O(4) = 1.964 Å) when the bridging OH is trans to a terminal hydroxo ligand. This is in agreement with the strong trans influence exerted by terminal oxo ligands.

The calculated IR spectrum for *dmPhe-I* and the experimental spectrum of complex **6** show a certain agreement. A weak band due to N−H stretching vibrations is expected at 3280 cm^{-1} (found at 3040 cm^{-1}), a strong absorption for the carboxylate stretching is expected at 1670 cm^{-1} (found at 1610 cm^{-1}) and strong bands for MoO$_2$ stretching vibrations are expected in the 947-965 cm^{-1} interval (found at 946, 916 and 903 cm^{-1}).

An approach for the polymerization of these dinuclear complexes was then attempted assuming the condensation of two terminal OH groups (23). This reaction leads to the formation of a Mo−O−Mo bridge that links two units.

$$\text{Mo−OH + HO−Mo} \longrightarrow \text{Mo−O−Mo + H}_2\text{O} \qquad (23)$$

The optimized structure for the *N,N*-dimethyl-L-phenylalanine complex (*dmPhe-I*) was used as a starting point for this purpose. Figure 61 reports the optimized structure for the oxo bridged tetramer (named *2·dmPhe-I*). Selected bond distances and angles are reported in table 26.
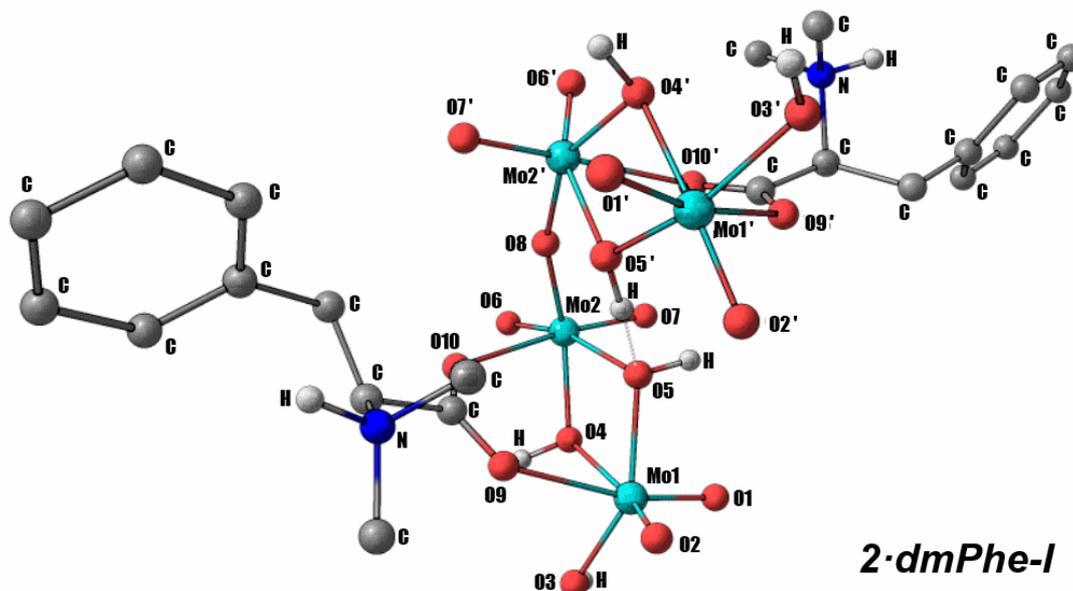
Fig. 61. Most stable optimized structure for the condensation reaction hypothesis. Carbon-bonded hydrogen atoms have been omitted for clarity ; corresponding Mo and O atoms in the two dinuclear units share the same number

In the tetrameric structure, the two Mo$_2$ units are held together not only by a bent oxygen bridge[v] (Mo(2)−O(8)−Mo(2') bond angle = 157 °) but also by a hydrogen bond between an OH bridging ligand of each dimer (one OH group is the donor and the other is the acceptor). This hydrogen bond does not substantially change the structure (with respect to *dmPhe-I*), but contributes to its stability. Even in this case, no intermolecular hydrogen bond involves the ammonium group.

The condensation reaction (24) is thermodynamically favoured in the gas phase, having an

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v The presence of a bent Mo−O−Mo bridge is supported also by IR characterization (see section 3.4)

energy difference of -21.9 kcal·mol^{-1}.[t]

Assuming successive condensation reactions, (25), an oxo-bridged coordination polymer (or oligomer) is obtained, which is representable with the short formula $\{Mo_2O_4(OH)_2(aaH)(\mu\text{-}O)\}_n \cdot H_2O$.

$$2\, Mo_2O_4(OH)_4((NMe_2)PheH) \longrightarrow \{Mo_2O_4(OH)_3((NMe_2)PheH)\}_2(\mu\text{-}O) + H_2O \quad (24)$$

$$n\, Mo_2O_4(OH)_4(aaH) \longrightarrow \{Mo_2O_4(OH)_2(aaH)(\mu\text{-}O)\}_n \cdot H_2O + (n\text{-}1)\, H_2O \quad (25)$$
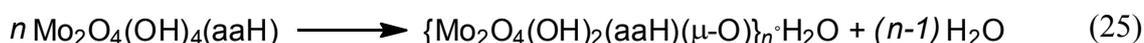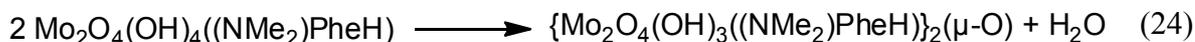
Therefore, complexes **1-6** may not be dinuclear (structure (a) in figure 62) but rather be composed of several dinuclear units condensed to form a chain (structure (b) in figure 62). The proposed polymeric nature also explains the general insolubility of these complexes in water and in common organic solvents (see section 3.6).
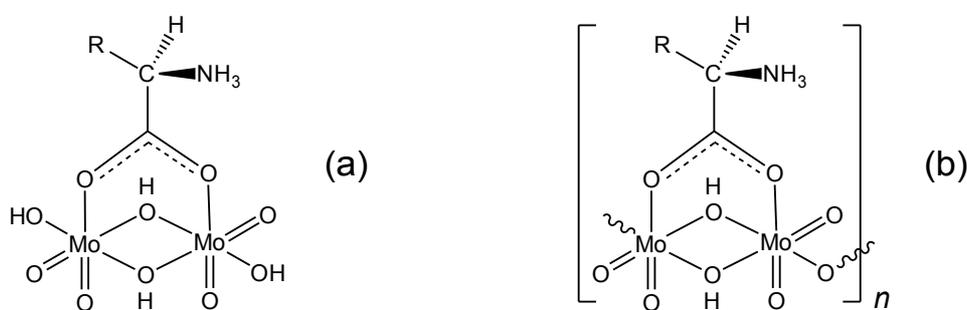
Fig. 62. Monomeric (a) and polymeric (b) formulations for the complexes **1-6**

It is interesting to make a comparison between the proposed structures and similar ones known in the literature. Only a small group of structurally-determined molybdenum(VI) compounds has a zwitterionic ligand involved in a bridging bidentate coordination with its carboxylate group.

This group include the heteropolymolybdates of general formula $[XMo_6O_{21}(O_2CRNH_3)_3]^{n-}$ (with X = VO, Se, Te, As, Sb, Bi and RP with R = OH, H, Me, Et),[101-103] that have been briefly mentioned in section 1.4. In these complexes, each *cis*-MoO$_2$ group is linked to a second one by two oxo bridging ligands and to a third one by one oxo bridging ligand. This give rise to a chain of three $[(Mo_2O_4(\mu\text{-}O)_2)(\mu\text{-}O)]$ dimers enclosed in a ring. The pair of molybdenum atoms bridged by two oxo ligands are also bridged by a zwitterionic α- (glycine, L-alanine, L-lysine), β- (β-alanine) or γ-amino acid (4-aminobutyric acid). The heteroatom X is located at the centre of this ring and it is coordinated to one oxo bridge for each Mo$_2$ dimer, giving it a tetrahedral arrangement. The structure of the anion in $K_2[HMo_6VO_{22}(GlyH)_3]$ is reported in figure 63(a).
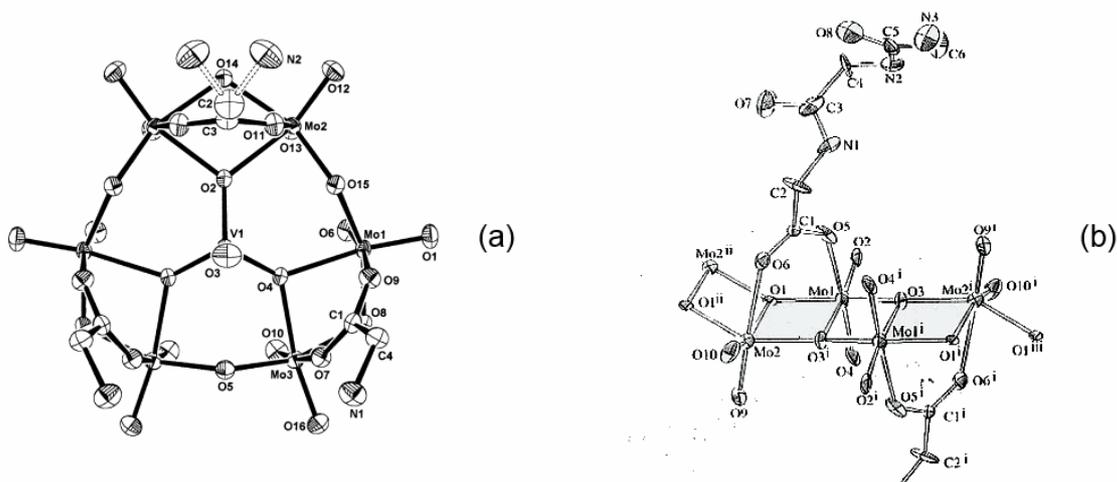
Fig. 63. (a) Crystal structure of the anion in $K_2[HMo_6VO_{22}(GlyH)_3)]$ (the hydrogen atom is omitted);[101] and (b) crystal structure of $\{[Mo_2O_6(Gly\text{-}Gly\text{-}Gly)]\cdot H_2O)\}_n$ [284]

Two neutral polymeric complexes of general formula $\{[Mo_2O_6(L)]\cdot H_2O)\}_n$, with L = nicotinic acid (3-carboxypyridine)[274] and glycylglycylglycine,[284] complete the aforementioned group of structurally-determined Mo(VI) compounds. The structure of the latter is reported in figure 63(b). In this case, the repeating unit consists of two *cis*-MoO_2 groups bridged by two oxo ligands and the carboxylate group of the zwitterionic ligand. Differently from the heteropolymolybdates, each Mo−$O_{bridging}$ unit is also part of a second four-membered ring with another Mo−$O_{bridging}$ unit of the adjacent dimer. This connection gives rise to an infinite rail-like chain of Mo_2O_2 units. This condensed structure preserves both the hexacoordination of molybdenum and the $Mo_2O_2(\mu\text{-}O)_2$ dimeric structure already seen in heteropolymolybdates.

It is interesting to note that all of these complexes contain $Mo_2O_4(\mu\text{-}O)_2$ dimers linked together by bridging oxo ligands. Basically, the heteropolyanions can be seen as a ring of three $Mo_2O_4(\mu\text{-}O)_2(LH\text{-}\kappa O,\kappa O')$ units linked by oxo bridges and held together by a central heteroatom, while the neutral compounds are built up of a chain of $Mo_2O_4(\mu\text{-}O)_2(LH\text{-}\kappa O,\kappa O')$ units with triply-coordinated bridging oxygens. It seems that the heteroatom works as a "centre of aggregation" for the $Mo_2O_4(\mu\text{-}O)_2$ units, giving rise to the Mo_6O_{21} ring. In absence of heteroatoms, these units links together in a similar way but forming an infinite chain polymer. This observation supports the hypothesis of the $\{Mo_2O_4(OH)_2(aaH)(\mu\text{-}O)\}_n$ structure proposed for complexes **1-6**.

Tab. 26. Selected calculated bond lengths (Å) and angles (°) for structures *Gly-I*, *Gly-II*, *dmPhe-I* and *2·dmPhe-I*

	Gly-I	*Gly-II*	*dmPhe-I*	*2·dmPhe-I*	
				Mo1,Mo2 unit	*Mo1',Mo2' unit*
Mo(1)–O(1)	1.704	1.699	1.710	1.708	1.711
Mo(2)–O(7)	1.706	1.691	1.707	1.720	1.723
Mo(1)–O(2)	1.706	1.705	1.713	1.708	1.706
Mo(2)–O(6)	1.690	1.765	1.710	1.722	1.709
Mo(1)–O(4)	2.363	2.263	2.323	2.400	2.319
Mo(1)–O(5)	2.076	2.089	2.041	2.099	2.039
Mo(2)–O(5)	2.573	2.130	2.270	2.237	2.354
Mo(2)–O(4)	1.964	2.050	2.098	2.013	2.084
Mo(1)–O(3)	1.914	1.904	1.960	1.923	1.950
Mo(2)–O(8)	2.031	1.899	1.919	1.915	1.887
Mo(1)–O(9)	2.418	2.572	2.310	2.315	2.358
Mo(2)–O(10)	2.346	2.582	2.350	2.315	2.311
O(1)–Mo(1)–O(2)	106.1	105.5	105.8	105.5	106.4
O(6)–Mo(2)–O(7)	104.1	105.0	104.7	105.2	105.1
O(2)–Mo(1)–O(4)	165.9	149.7	160.1	162.2	165.9
O(2)–Mo(1)–O(5)	106.0	91.6	94.6	97.1	97.6
O(6)–Mo(2)–O(5)	169.5	147.1	158.3	158.2	161.0
O(6)–Mo(2)–O(4)	105.0	91.1	97.9	94.6	101.6
O(2)–Mo(1)–O(3)	97.4	104.7	103.5	104.8	102.0
O(6)–Mo(2)–O(8)	105.3	107.1	105.0	103.4	103.0
O(2)–Mo(1)–O(9)	83.5	86.2	89.3	89.3	88.9
O(6)–Mo(2)–O(10)	83.9	79.5	83.5	84.2	82.1
O(1)–Mo(1)–O(4)	87.0	97.7	89.7	88.7	91.5
O(1)–Mo(1)–O(5)	101.6	100.9	101.0	98.7	92.9
O(7)–Mo(2)–O(5)	85.3	102.8	94.3	94.2	84.3
O(7)–Mo(2)–O(4)	93.2	104.3	94.1	93.0	98.0
O(1)–Mo(1)–O(3)	102.6	100.9	96.8	98.5	103.3
O(7)–Mo(1)–O(8)	103.0	101.8	102.7	104.2	102.1
O(1)–Mo(1)–O(9)	170.1	167.4	164.4	165.0	165.6
O(7)–Mo(2)–O(10)	166.2	173.2	168.2	167.6	166.9
O(3)–Mo(1)–O(4)	74.2	86.8	85.0	83.0	79.3
O(3)–Mo(1)–O(5)	140.0	146.1	148.8	147.3	147.6
O(8)–Mo(2)–O(5)	76.6	83.6	81.9		
O(8)–Mo(2)–O(4)	140.8	146.0	148.3		
O(3)–Mo(1)–O(9)	77.9	70.6	75.1	75.6	85.5
O(8)–Mo(2)–O(10)	83.9	71.9	83.2	81.6	76.9
O(5)–Mo(1)–O(9)	73.0	83.1	81.3	77.0	76.1
O(5)–Mo(2)–O(10)	83.6	73.0	76.5	76.2	81.2
O(4)–Mo(1)–O(9)	84.7	72.9	76.2	80.8	79.1
O(4)–Mo(2)–O(10)	74.4	82.0	76.2	76.6	76.9
O(4)–Mo(1)–O(5)	75.7	67.9	69.8	69.8	71.3
O(4)–Mo(2)–O(5)	69.3	64.8	70.0	71.1	70.5
Mo(2)–O(8)–Mo(2')				157.8	

Section 3.6 - Behaviour and solubility in water and in organic media

Acids and bases in aqueous solution

Compounds **1-6** were stirred in water at room temperature for several hours, resulting in colourless pH ≈ 3 solutions and colourless solids. The dissolution of $Mo_2O_4(OH)_4(aaH)$ occurred only to a minimum extent, since:

- The ^1H NMR spectrum of the solution showed only very weak signals for the amino acid (verified for **1-4** and **6**)

- The undissolved solid, corresponding to the starting reagent, was collected by filtration in almost quantitative yield (verified for **1** and **6**)

Similarly, complexes **1-6** were not dissolved by 1 M HNO_3 or HCl. A more acidic medium (4 M HCl or HNO_3) was able to dissolve rapidly these compounds, affording colourless solutions. The dissolution of **6** by 4 M HCl was slow at room temperature but rapid when heated at 90 °C or by adding 37 % HCl. These solutions probably contained the protonated uncomplexed form of the amino acid (aaH_2^+) and $[MoO_2]^{2+}$ or $[MoO(OH)]^+$ aquoions, which are the stablest species in this strong acidic medium (see section 1.1).

The behaviour of $Mo_2O_4(OH)_4(GlyH)$ towards H_2O and OH^- at room temperature was studied by monitoring the pH of the solution after each base addition; the quantity of base added being expressed as $OH^-/Mo_2O_4(OH)_4(GlyH)$ (or simply OH/Mo_2) molar ratio. The time profile of pH after some of the base additions is reported in figure 64.

When $Mo_2O_4(OH)_4(GlyH)$ was stirred in water, the pH of the solution rapidly decreased and then stabilized around a value of 3. This suspension was titrated with a sodium hydroxide solution. After additions of base up to $OH/Mo_2 = 1.26$, the pH was slowly stabilized around a value of 4.6 (e.g. see time profile of pH for the $OH/Mo_2 = 1.0$ addition in figure 64) and a large part of the solid was dissolved. A further addition of base (molar ratio = 1.44) completely dissolved the solid and the pH stabilized at 4.83. From this moment onwards, the pH of the solution reached a steady value soon after the NaOH addition, suggesting that the slow reaction involving OH^- has gone to completion. Figure 65 reports the the equilibrium pH values after each base addition.
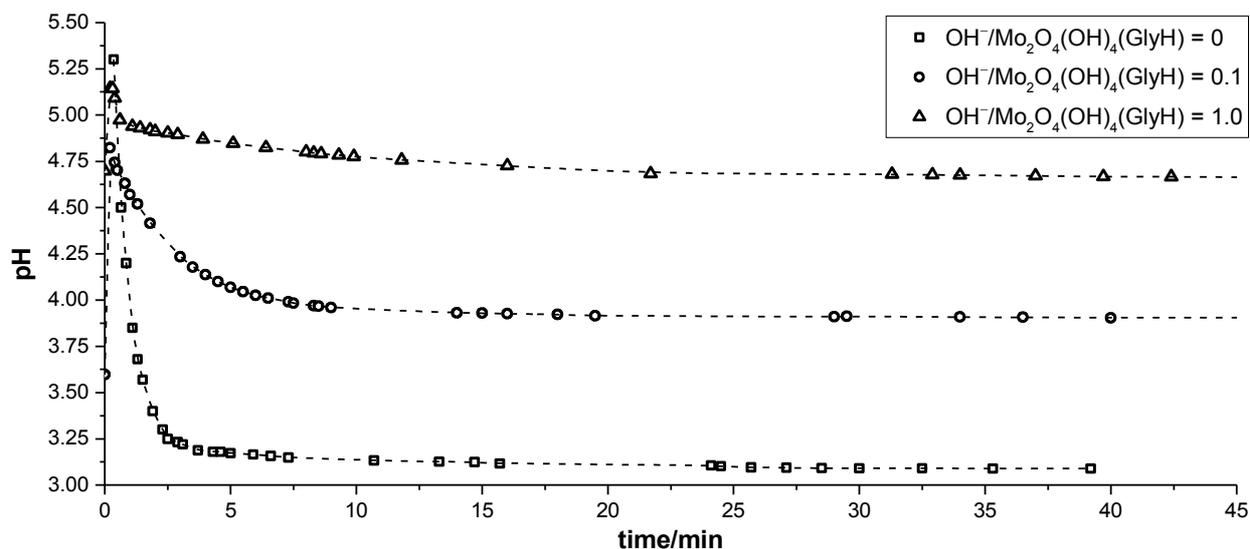
Fig. 64. The profile of pH vs.time for a $Mo_2O_4(OH)_4(GlyH)$ suspension in water (squares) and after reaching a $OH^-/Mo_2O_4(OH)_4(GlyH)$ molar ratio of 0.1 (circles) and 1.0 (triangles)
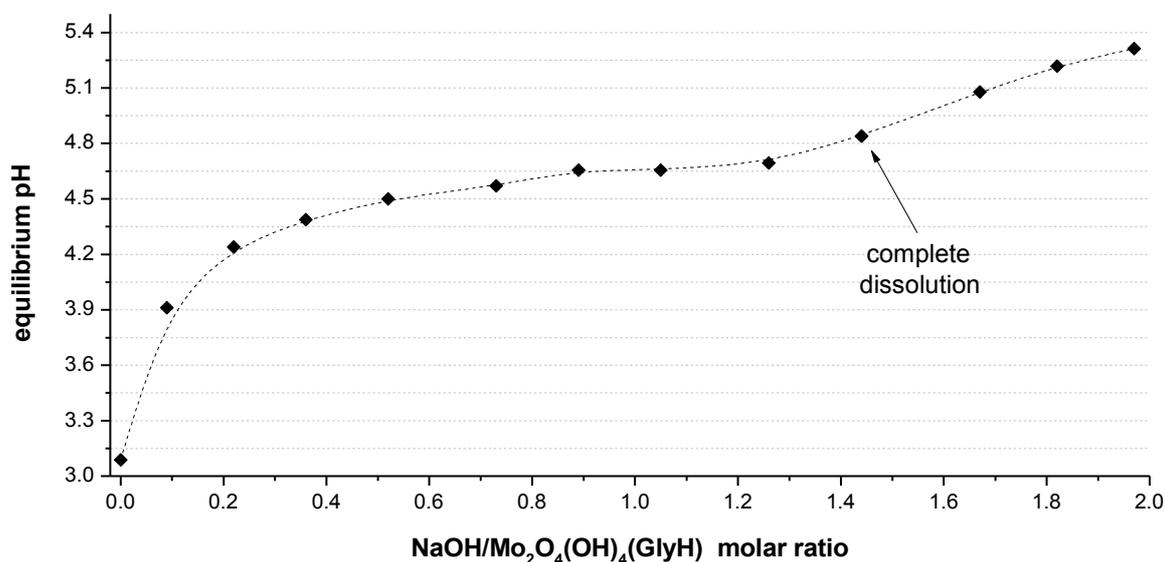
Fig. 65. Equilibrium pH values after each NaOH addition in an aqueous suspension of $Mo_2O_4(OH)_4(GlyH)$

After a final addition, which led to $OH/Mo_2 = 1.95$, an aliquot of the resulting colourless solution was transferred in a flask and a crystalline solid was obtained from it after complete solvent removal under vacuum. The IR spectrum of this solid is superimposable to that of glycine in the 1000-1650 cm^{-1} interval, while the Mo–O stretching region is similar to the one found in the spectrum of $Na_2MoO_4 \cdot 2H_2O$. The sublimation of a solid, probably MoO_3,[285] was observed when the test tube containing the product was heated using a Bunsen burner. These observations suggest that a co-precipitate of glycine and an inorganic molybdate was obtained (probably $Na_2MoO_4 + MoO_3 \cdot nH_2O$ since only 2 equivalents of NaOH were added). In turn, this indicates that the glycine in solution was not complexed: the addition of NaOH led to the hydrolysis of $Mo_2O_4(OH)_4(GlyH)$, according to reaction (26).

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$$\text{Mo}_2\text{O}_4(\text{OH})_4(\text{GlyH}) + 2\,\text{OH}^- \longrightarrow 2\,[\text{MoO}_4]^{2-} + \text{GlyH} + 2\,\text{H}_3\text{O}^+ \qquad (26)$$
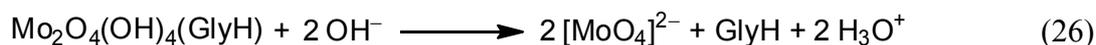
The solution with pH = 5.25 thus obtained was titrated with a HNO$_3$ solution. The pH of the solution reached the equilibrium value immediately after each addition (< 1 minute) and dropped to 2.65 when the 70 % of the NaOH previously added was neutralized. With a further addition, the equimolarity was reached (HNO$_3$ = NaOH) and pH dropped to 2.01. Under these conditions Mo$_2$O$_4$(OH)$_4$(GlyH) was formed again and it was recovered in a 95 % yield, compared to the initial amount. The pH of the solution showed the usual time profile during the solid formation (as described in section 3.2). This proves that the formation of Mo$_2$O$_4$(OH)$_4$(GlyH) is completely reversible in aqueous solution and that the presence of the amino acid adduct depends on the pH (see figure 66).

$$2\,[\text{MoO}_4]^{2-} + \text{GlyH} \quad \underset{\text{OH}^-}{\overset{\text{H}^+}{\rightleftharpoons}} \quad \text{Mo}_2\text{O}_4(\text{OH})_4(\text{GlyH})$$
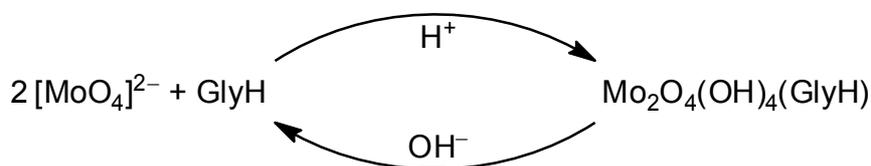
Fig. 66. Formation and dissolution of Mo$_2$O$_4$(OH)$_4$(GlyH) in aqueous solution

Alcohols and acetonitrile

Complexes **1-6** were poorly soluble or insoluble, at room temperature, in alcohols (MeOH, EtOH, ^{i}PrOH) and in acetonitrile. This was verified by stirring for 24 hours Mo$_2$O$_4$(OH)$_4$(ProH) in ROH (R = Me, Et, ^{i}Pr) and Mo$_2$O$_4$(OH)$_4$(GlyH) in acetonitrile.

The UV-Vis spectrum of EtOH and ^{i}PrOH solutions showed no absorption in the range 200-1100 cm^{-1} while a strong band centered at 225 cm^{-1} appeared for the MeOH solution. Ligand-to-metal charge-transfer bands are typical for d^0 metal complexes[286,287] and this absorption may be ascribed to a [MoO$_x$] group in solution.[288] Therefore, a small amount of Mo$_2$O$_4$(OH)$_4$(ProH) was dissolved in MeOH at room temperature. The undissolved solid (collected by filtration) corresponded to the starting reagent for each alcohol: thus no ligand-exchange reaction occurred in the solid state.

The compound Mo$_2$O$_4$(OH)$_4$(GlyH) was recovered in 86 % yield from the acetonitrile suspension and thus showed a small solubility also in this polar aprotic solvent.

A different situation was observed at higher temperatures. Complex Mo$_2$O$_4$(OH)$_4$(PheH) was refluxed in MeOH and the resulting colourless solution was allowed to evaporate slowly. Under these conditions, a blue colour appeared and its intensity increased with time. GC-MS revealed a major presence of the methyl ester of L-phenylalanine, together with smaller amounts of methyl formate and benzonitrile.
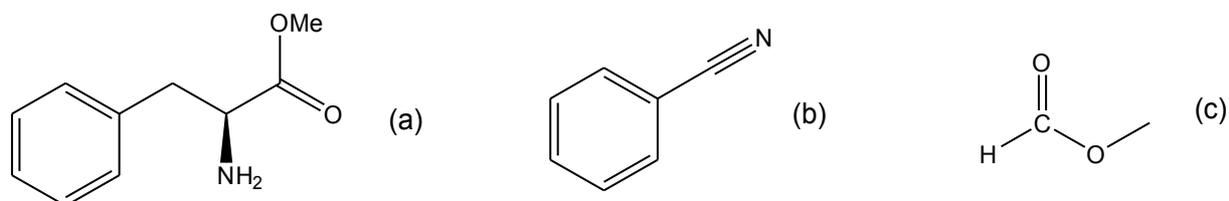
Fig. 67. Main products identified with GC-MS: (a) L-phenylalanine methyl ester, (b) benzonitrile and (c) methyl formate

These last two are the oxidation products of methanol and L-phenylalanine, respectively, and may account for the reduction of Mo(VI) to Mo(V).[193] The formation of an organic nitrile and the appearance of the blue colour was already observed during a reaction of L-leucine with ammonium heptamolybdate (see section 3.1). A blue solid was obtained after complete solvent removal. This was dissolved in D_2O and the presence of the methyl ester of L-phenylalanine along with L-phenylalanine (1.3 : 1 molar ratio) was confirmed by NMR spectroscopy.

A suspension of $Mo_2O_4(OH)_4(PheH)$ in a water / methanol mixed solvent (2 : 1 in volume; pH adjusted to 2 with HNO_3) resulted in a colourless solution after 6 hours under refluxing conditions. A pale blue solution and $Mo_2O_4(OH)_4(PheH)$ as a microcrystalline solid were obtained after several days of slow evaporation. GC-MS of the solution revealed also in this case the presence of CO_2 and benzonitrile.

In conclusion, complex **2** was dissolved with reaction in methanol and in a water / methanol pH = 2 solution under refluxing conditions. In the first case the redox reaction that involves molybdenum and the esterification of the amino acid took place. In the second case instead $Mo_2O_4(OH)_4(PheH)$ was reobtained from the solution and thus the redox reaction leading to Mo(V) and benzonitrile, probably occurred in a smaller extent. However this observation (having reobtained complex **2** from the solution) does not reveal whether the structure of the complex is maintained in solution or if any reversible reaction accompanies the dissolution (i.e. the situation previously described with $Mo_2O_4(OH)_4(GlyH)$ and OH^-).

Dimethyl sulphoxide

Complexes **1-4** and **6** dissolved in DMSO with yellow colour. The dissolution of $Mo_2O_4(OH)_4(GlyH)$ was slow at room temperature but rapid when heating (50-100 °C). Once the solution was cooled to room temperature, the re-precipitation of a solid was not observed.

The ^{13}C NMR spectra (in DMSO-d_6) of these solutions generally showed more than one group of signals (one, two and three groups of signals with different intensity for compound **1**, compounds **3** and **6** and compounds **2** and **4**, respectively) attributable to the amino acid. The chemical shift values of the most intense group of signals were very similar to those found in the

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solid state (e.g. δ = 169-172 ppm for the carboxylic carbon). The less intense groups of signals were characterized by more deshielded chemical shifts (e.g. δ = 177-179 ppm for the carboxylic carbon).

[1]H spectra showed a signal at ca. 4.30 ppm which could be ascribed to a molecule of molybdenum-coordinated DMSO.[289] Dimethyl sulphoxide (DMSO) is indeed a common ligand in coordination chemistry[290] and it is plausible to assume that the dissolution of $Mo_2O_4(OH)_4(aaH)$ in DMSO is accompanied by ligand substitution reactions. In this connection, it is noteworthy that glycine has a poor solubility in DMSO[291] (and the same behaviour can be assumed for the other amino acids) but no formation of solid was observed on treatment of the molybdenum complexes with DMSO. This suggests that the amino acid remains coordinated to molybdenum even in the presence of a strongly competitive and neutral ligand such as DMSO.

Section 3.7 - Catalytic activity

This section describes the catalytic activity of complexes **1-6** in the oxidation of cyclohexene (Cy) with hydrogen peroxide.

A brief description of catalytic oxidations of olefins, in particular cyclohexene, has been provided in section 1.6. Table 27 shows experimental conditions and products obtained in some molybdenum(VI)-catalysed oxidations of cyclohexene with hydrogen peroxide. Most of these reactions have been carried out at 60-80 °C in excess of hydrogen peroxide. The use of aqueous solutions of H_2O_2 and chlorinated solvents caused the formation of a biphasic system. Alcohols and acetonitrile have been more frequently used because they are miscible both with water and with cyclohexene. Alcohols, however, especially methanol and ethanol, have often caused the formation of 2-alkoxycyclohexanol by reacting with 1,2-cyclohexanediol.

Therefore, acetonitrile was chosen as the solvent. The reactions were carried out with a oxidant/substrate molar ratio of 3.50 at 65 °C. This means that the effect of the amount of H_2O_2 and temperature was not investigated.

In order to select the amount of catalytic precursor and the reaction time, reactions with varying amounts of $Mo_2O_4(OH)_4(GlyH)$ were monitored by NMR spectroscopy. In such experimental conditions, $Mo_2O_4(OH)_4(GlyH)$ was dissolved in a few minutes and yellow solutions resulted. Figure 68 reports the time profile of cyclohexene conversion for three reactions with a different initial cyclohexene/molybdenum molar ratio (*R*).[w]
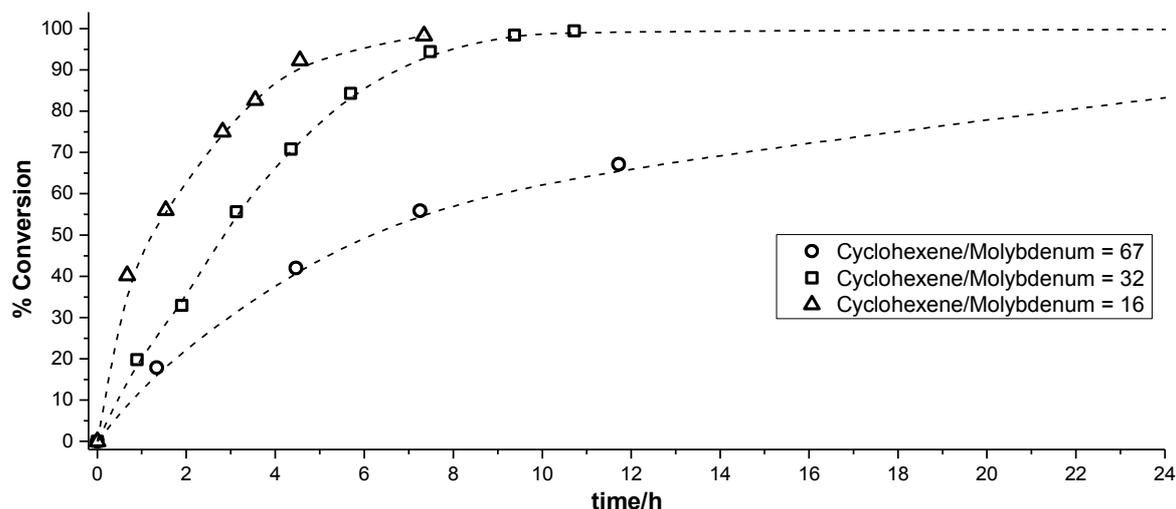
Fig. 68. Conversion of cyclohexene as a function of time for reactions with a cyclohexene/molybdenum molar ratio of 67 (circles), 32 (squares) and 16 (triangles)

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w For the sake of simplicity, the initial cyclohexene/molybdenum molar ratio will be indicated with *R* henceforth

Tab. 27. Cyclohexene oxidation with hydrogen peroxide and Mo(VI) complexes

Reaction Conditions*	% Conversion	% Selectivity [§]					Ref.
		CyO	Cy(OH)$_2$	Cy(OH)(OR)	(Cy−H)OH	(Cy−2H)O	
[MoO(O$_2$)(4,4'-bipy)]$_n$ H$_2$O$_2$/Cy = 2.7 ; cat. 18 w% RT; t = 12 h; H$_2$O / CH$_2$Cl$_2$ (biphasic)	99	99					174
MoO$_2$L$_n$/polystyrene, L = imidazole derivative H$_2$O$_2$/Cy = 2.0 ; cat. 4.3 w% T = 80 °C; t = 6 h; MeCN	66	2	84			12	171
CpMo(CO)$_3$(C≡CPh) H$_2$O$_2$/Cy = 2.0 ; Cy/Mo = 500 T = 65 °C; t = 48 h; MeOH / ^{t}BuOH	91-95		42 (cis-; MeOH) 86 (cis-; ^{t}BuOH)	9 (^{t}BuOH) 48 (MeOH)	0-4	5-6	173
MeCN / CH$_2$Cl$_2$ / CHCl$_3$ / CCl$_4$	67-72		60-68 (cis-)		0-17	15-23	
MoO(O$_2$)$_2$(DMF)$_2$/poly(4-vinylpyridine) H$_2$O$_2$/Cy = 6.3 ; cat. 35 w% T = 60 °C; t = 24 h; EtOH	100	97	3				172
(PPh$_4$)$_2$[MoO(O$_2$)$_2$L] + NaHCO$_3$, L = benzoic acid derivative H$_2$O$_2$/Cy = 3-6 ; Cy/Mo = 10^3-10^4 RT; t = 1 h; CH$_3$CN	99	93-99					169
MoO$_3$, Na$_4$Mo$_8$O$_{26}$ and [Bu$_4$N][Mo$_6$O$_{19}$] H$_2$O$_2$/Cy = 1.5 ; Cy/Mo = 40 T = 60 °C; t = 18h; Me$_2$CO	17	5	95				167
MeOH / EtOH / ^{i}PrOH / ^{t}BuOH	65-79	1-2	12-99	0-87			
CpMo(CO)$_3$(C≡CPh) H$_2$O$_2$/Cy = 2.0 ; Cy/Mo = 2000 T = 80 °C; t = 9 h; ^{t}BuOH	95	0	91 (cis-)		9		164

* Catalyst precursor, oxidant/substrate molar ratio, substrate/catalyst molar ratio (homogeneous catalysis) or catalyst/substrate percent mass ratio (heterogeneous catalysis), temperature, time and solvent

[§] The main products obtained were cyclohexene oxide (CyO), 1,2-cyclohexanediol (Cy(OH)$_2$), 2-cyclohexenone ((Cy−2H)O), 2-cyclohexenol ((Cy−H)OH) and 2-alkoxycyclohexanol (Cy(OH)(OR))

The conversion reached 100 % after several hours. As expected, the rate was faster on increasing the concentration of molybdenum, the other conditions being similar. An almost quantitative conversion was obtained after ca. 6 hours in the reaction with $R = 16$.

The main oxidation product identified was *trans*-1,2-cyclohexanediol (*trans*-Cy(OH)$_2$) along with a smaller amount of its diastereomer, *cis*-1,2-cyclohexanediol (*cis*-Cy(OH)$_2$) as shown in figure 69.
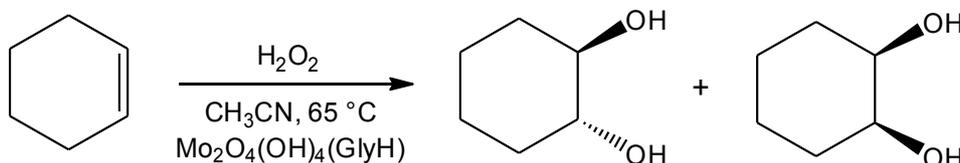
Fig. 69. The main products obtained from the oxidation of cyclohexene under the selected catalytic conditions

Figure 70 shows the yield of *trans*-Cy(OH)$_2$ as a function of time. As it can be seen, the yield increased in the early stages of the reaction and then decreased. A similar behaviour was observed for *cis*-Cy(OH)$_2$, although on a smaller scale (this product never reached a 10 % yield).

A direct correlation was observed between the initial rate of formation of *trans*-Cy(OH)$_2$ and the value of R.[x]
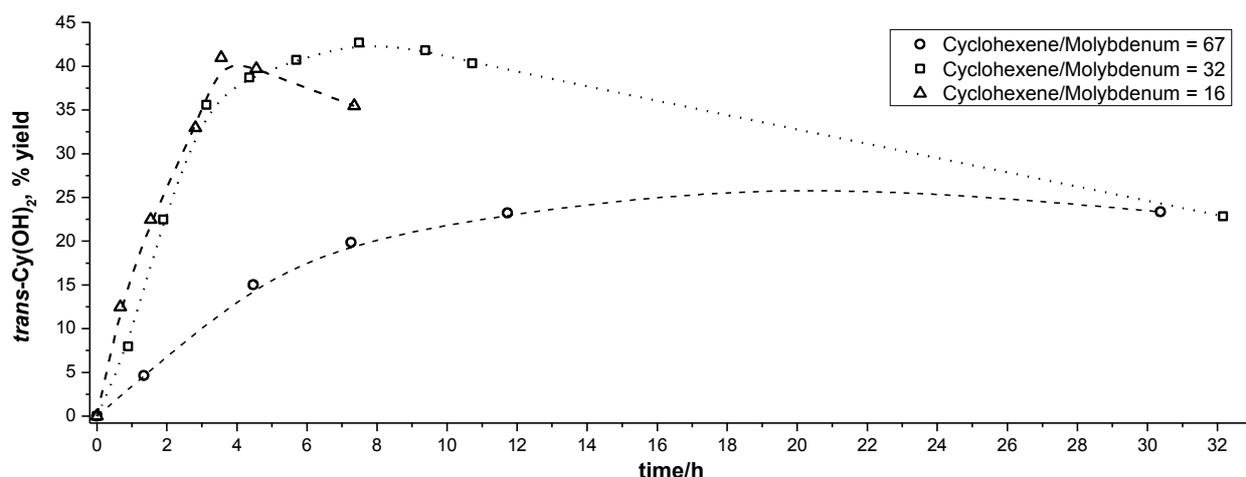
Fig. 70. Yield of *trans*-Cy(OH)$_2$ as a function of time for reactions with a cyclohexene/molybdenum molar ratio of 67 (circles), 32 (squares) and 16 (triangles)

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x The *turnover frequency* (TOF) is defined as the molecules reacting per active site in unit time.[194] This quantity can be calculated using equation (27) and knowing the number of active sites, n_{cat}, and the molecules of product formed, n_{prod}, at a given reaction time, t. By expressing the moles of product as yield, Y_{prod}, and denoting with R the initial substrate/molybdenum molar ratio, equation (28) is obtained. At the beginning of the reaction, the yield vs. time can be considered linear (see the first two points for each reaction in figure 71). Therefore, the initial turnover frequency (indicated as TOF^0) can be expressed by equation (29), in which s is the slope of the yield vs. time straight line. The values of s were linearly correlated to the values of 1/R for the three reactions ($R^2 = 0.9996$) and TOF^0 = 3.2 h^{-1} was obtained.

$$TOF = \frac{n_{prod}}{n_{cat} \cdot t} \quad (27) \qquad TOF = \frac{R \cdot Y_{prod}}{t} \quad (28) \qquad TOF^0 = R \cdot s \quad (29)$$

The decrease of cyclohexanediols may be due to ring opening reactions. It has been recently reported that 2,2'-oxydicyclohexanol (the monocondensation product of $Cy(OH)_2$) and dicarboxylic acids were observed as main oxidation products of *trans*-$Cy(OH)_2$ when $Ru(OH)_3$ and P / Mo / V polyoxometalates were used as catalysts.[292]

In order to get a better understanding of this catalytic system, blank reactions were carried out (#1–#3). In addition, a reaction was performed using $Na_2MoO_4 \cdot 2H_2O$ instead of $Mo_2O_4(OH)_4(GlyH)$ (#4). These reactions were allowed to go on until complete conversion (112 hours). Results are summarized in table 28.

Tab. 28. Reactions without $Mo_2O_4(OH)_4(GlyH)$ (#1), cyclohexene (#2), hydrogen peroxide (#3) and with $Na_2MoO_4 \cdot 2H_2O$ as catalyst precursor (#4)

Reaction	Molybdenum compound	Substrate	Oxidant	Oxidation products identified [§]
#1	-	Cy	H_2O_2	*trans*-$Cy(OH)_2$ (27 %), acetamide
#2	$Mo_2O_4(OH)_4(GlyH)$	-	H_2O_2	Oxamide
#3	$Mo_2O_4(OH)_4(GlyH)$	Cy	-	-
#4	$Na_2MoO_4 \cdot 2H_2O$	Cy	H_2O_2	2-Cyclohexenone (30 %), acetamide

[§] Percent yields reported for the oxidation products of cyclohexene are low due to possible losses caused by the long reaction time

In the metal-free reaction, *trans*-$Cy(OH)_2$ was identified as the main oxidation product of cyclohexene. However, this product was formed only for 1 % after 3 hours. This means that the whole *trans*-$Cy(OH)_2$ formed in the presence of $Mo_2O_4(OH)_4(GlyH)$ can be ascribed to the catalysed pathway.

Oxamide, $(CONH_2)_2$, was the only product obtained from the reaction in the absence of cyclohexene. The formation of this product is due to the oxidation of acetonitrile. This product was also identified in the previously mentioned reactions (with $R = 32$ and $R = 16$) when the conversion of cyclohexene was almost complete. In the literature, oxamide has been prepared by oxidation with hydrogen peroxide of hydrogen cyanide in aqueous solution.[293,294] Moreover, it is known that acetonitrile can be oxidized in the presence of a vanadium oxide based catalyst[295] to glycolonitrile which decomposes to hydrogen cyanide and formaldehyde.[296] Thus the formation of oxamide may be explained according to the scheme in figure 71.
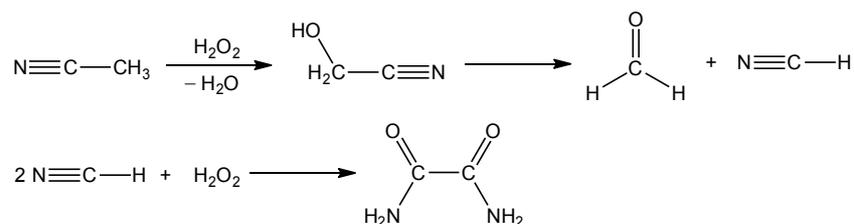
Fig. 71. Proposed scheme of reactions for the formation of oxamide

No other organic product, except cyclohexene, was identified in the reaction mixture without H_2O_2, thus suggesting that an oxygen transfer reaction[45] from the dioxomolybdenum complex to the alkene did not occur under these conditions. It is interesting to note that, in this case, $Mo_2O_4(OH)_4(GlyH)$ was not completely dissolved even after 40 hours (a yellow solution resulted after 112 hours). This indicates that the rapid dissolution of $Mo_2O_4(OH)_4(GlyH)$ observed at the beginning of catalytic reactions, was due to a reaction with H_2O_2.

The activity of sodium molybdate under these conditions was different from that of $Mo_2O_4(OH)_4(GlyH)$. Soon after its addition to the acetonitrile solution of H_2O_2 and cyclohexene at 65 °C, $Na_2MoO_4·2H_2O$ decomposed to a red oily product (which was slowly dissolved in the reaction mixture) and the formation of a gaseous product was observed. 2-Cyclohexenone was identified as the only oxidation product of cyclohexene. This product, obtained as a result of allylic oxidation of cyclohexene[297] (see figure 72), was not present in reactions with $Mo_2O_4(OH)_4(GlyH)$. Acetamide, the hydrolysis product of acetonitrile, was obtained as a crystalline sublimate when the final reaction mixture was distilled under vacuum at 40 °C.
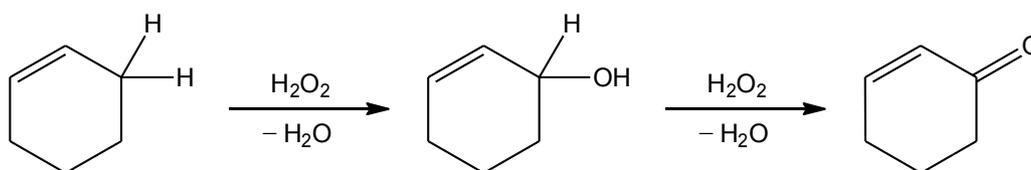
Fig. 72. The allylic oxidation of cyclohexene leads first to 2-cyclohexenol and then to 2-cyclohexenone

The catalytic activity of complexes containing chiral amino acids (**2-6**) was finally investigated. Previous reactions with $Mo_2O_4(OH)_4(GlyH)$ have shown that a faster conversion of cyclohexene is obtained with $R = 16$ and that the maximum yield of *trans*-$Cy(OH)_2$ is obtained after ca. 3 hours. These experimental conditions were thus adopted.

After a reaction time of 3 hours, the resulting yellow solution was cooled down to room temperature and volatiles were removed in vacuum. Diethyl ether and NaCl were added to the residue. Diols extracted in the organic phase were determined quantitatively by GC-FID. The enantiomeric excess of (1S,2S)-*trans*-1,2-cyclohexanediol was determined by polarimetric analysis. Table 29 shows the results of these reactions, together with one carried out with the achiral $Mo_2O_4(OH)_4(GlyH)$ for comparison.

For each reaction, gas chromatography revealed the presence of *cis*-$Cy(OH)_2$, *trans*-$Cy(OH)_2$ and other three compounds in a very low amount (their relative area is ca. 1-7 % compared to 13-24 % for *cis*-$Cy(OH)_2$ and 100 % assigned to *trans*-$Cy(OH)_2$).

Tab. 29. Catalytic activity of complexes **1-6** towards the oxidation of cyclohexene

Catalyst precursor	Cy, NMR % conversion	trans-Cy(OH)₂, GC % Yield	cis-Cy(OH)₂, GC % Yield	trans- + cis- % Selectivity	Diastereomeric excess %	Enantiomeric excess %
1	77	31.7	7.7	51	70	
2	70	33.4	5.7	56	71	5
3	67	26.8	6.4	50	61	1
4	63	31.6	5.0	58	73	5
5	67	23.1	4.8	42	66	3
6	79	31.6	4.3	45	76	5

As can be seen from table 29, the differences in catalytic activity between complexes **1-6** are not remarkable. Reactions with L-phenylalanine and L-methionine complexes showed the highest selectivity towards the dihydroxylation of cyclohexene (56-58 %). The reaction with complex **6** had a low selectivity for diols (45 %) but the highest diastereomeric excess (76 %). A small enantiomeric excess of (1S,2S)-*trans*-1,2-cyclohexanediol (1-5 %) was generally observed when using chiral complexes (**2-6**). This means that the amino acid is bonded to molybdenum in the catalytic active species, but it does not cause a good asymmetric induction under these experimental conditions.

For each reaction, a yellow solid was obtained after removal of the diethyl ether phase (extraction step). These products showed two strong bands around 960 cm^{-1} and 862 cm^{-1} (a third absorption around 900 cm^{-1} is present for the reactions with **4** and **5**), which are typical for a molybdenum oxoperoxo complex ([MoO(O$_2$)$_x$] moiety).[53]

Conclusions and future perspectives

Molybdenum(VI) complexes with hydrophobic side-chain α-amino acids (glycine [**1**], L-phenylalanine [**2**], L-leucine [**3**], L-methionine [**4**], L-proline [**5**] and *N,N*-dimethyl-L-phenylalanine [**6**]) have been prepared in high yield, as colourless solids, from acidic aqueous solutions. Sodium molybdate, ammonium molybdate and hexaammonium heptamolybdate have been used as molybdenum(VI) sources. The preparation of **1-6**, in various experimental conditions, has been described together with informations obtained by monitoring the pH of the reaction during their formation.

Analytical and spectroscopic characterization, supported by DFT calculations, suggested the formation, according to reaction (30), of dinuclear neutral dioxomolybdenum(VI) complexes with one zwitterionic α-amino acidic ligand having the general formula $[(MoO_2(OH))_2(\mu\text{-}OH)_2(\mu\text{-}(O_2CCH(NH_3)R\text{-}\kappa O,\kappa O'))]$. The two $[MoO_2]^{2+}$ groups are held together by two bridging OH ligands and the carboxylate group of the α-amino acid, which is involved in a bidentate bridging coordination. Two terminal OH groups, one for each metal, complete the hexavalent coordination sphere of molybdenum and balance the remaining positive ionic charge, leading to the structure (a) reported in figure 73.

The general insolubility in water and in common organic solvents suggests that these complexes may have a higher nuclearity. The condensation reaction (31) between two terminal –OH groups leads to the formation of the oxo-bridged coordination polymer (b) reported in figure 73, which is representable with the short formula $\{Mo_2O_4(OH)_2(aaH)(\mu\text{-}O)\}_n \cdot H_2O$. This is in agreement with DFT calculations.

The catalytic activity of the synthesized compounds towards the oxidation of cyclohexene in acetonitrile with hydrogen peroxide has been tested. 1,2-Cyclohexanediols were obtained as major products (42-58 % selectivity) with a good diastereoselectivity (ca. 70 %) for the *trans*- isomer after 3 hours at 65 °C.

$$4\,H^+ + 2\,[MoO_4]^{2-} + aaH \longrightarrow Mo_2O_4(OH)_4(aaH) \tag{30}$$

$$n\,Mo_2O_4(OH)_4(aaH) \longrightarrow \{Mo_2O_4(OH)_2(aaH)(\mu\text{-}O)\}_n \cdot H_2O + (n\text{-}1)\,H_2O \tag{31}$$
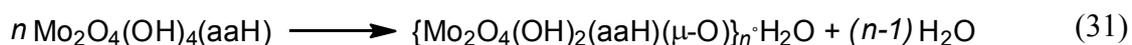
Fig. 73. Monomeric (a) and polymeric (b) formulations for the synthesized complexes

The experience about the formation and characterization of Mo(VI)-amino acids complexes obtained in this Thesis, can be exploited for the synthesis and characterization of new complexes of early transition metals in high oxidation state with natural ligands.

Groups 5 and 6 metals in their maximum oxidation state have a very similar chemistry which is dominated by oxo ligands.[1] A considerable number of oxo complexes has been prepared[48] and many of them have been used in organic synthesis as stoichiometric reagents (oxygen-atom transfer reaction)[45] or catalysts[298] (es. oxidation of alkenes, alcohols, sulphides...). Oxo species of vanadium, molybdenum and tungsten have also been found in the prosthetic group of various enzymes.[299,300] Tantalum and Niobium have no biological role, nevertheless these metals are highly biocompatible.[301] Also molybdenum salts are considered to be biocompatible.[302]

α-Amino acids (and their derivatives), monosaccharides and other small organic molecules such as nitrogen bases and α-hydroxy acids (lactic acid, ascorbic acid...) play a key role in various biochemical processes.[78] Their reactivity towards Group 5 and Group 6 oxometallates is quite unexplored, with the exception of Vanadium, due to its higher biological importance.[303]

The study of reactions between Group 5 and Group 6 oxometallates with biologically relevant molecules may represent an important contribution to the oxometallate chemistry and be useful to a better knowledge of the biological role of these metals.

In addition, these complexes can be used for catalytic oxidations and - in case of a good catalytic activity - they may be preferable to other oxo complexes used as catalysts (such as the osmium derivatives used in the Sharpless asymmetic dihydroxylation[149]), being synthesized from cheap and environmentally acceptable starting materials.

Bibliography

1.	Greenwood, N. N.; Earnshaw, A., *Chemistry of the Elements*. 2nd ed.; Butterworth-Heinemann: 1997.
2.	Blake, A. B.; Cotton, F. A., *J. Am. Chem. Soc.* **1964,** *86*, 3024.
3.	Mitchell, P. C. H., *Q. Rev. Chem. Soc.* **1966,** *20*, 103.
4.	Haight, G. P.; Boston, D. R., *J. Less. Common Met.* **1974,** *36*, 95.
5.	Tucci, G. C.; Donhaue, J. P.; Holm, R. H., *Inorg. Chem.* **1998,** *37*, 1602.
6.	Pau, R. N.; Lawson, D. N., *Metal ions in biological systems*. Sigel A.; Sigel. H. ed.; New York, 2002; Vol. 39.
7.	Holm, R. H.; Berg, J. M., *Acc. Chem. Res.* **1986,** *19*, 363.
8.	Hille, R.; Sprecher, H., *J. Biol. Chem.* **1987,** *262*, 10914.
9.	Emsley, J., *Nature's Building Blocks*. Oxford University Press: Oxford, 2001.
10.	Collison, D.; Garner, C. D.; Joule, J. A., *Chem. Soc. Rev.* **1996**, 25.
11.	Schultz, B. E.; Gheller, S. F.; Muetterties, M. C.; Scott, M. J.; Holm, R. H., *J. Am. Chem. Soc.* **1993,** *115*, 2714.
12.	Enroth, C.; Eger, B. T.; Okamoto, K.; Nishino, T.; Nishino, T.; Pai, E. F., *Proceedings of the National Academy of Sciences* **2000,** *97*, 10723.
13.	Grasselli, R. K., *Catal. Today* **1999,** *49*, 141.
14.	Cross, R. J.; Newman, P. D.; Peacock, R. D.; Stirling, D., *J. Mol. Catal.* **1999,** *144*, 273.
15.	Ivin, K. J.; Mol, J. C., *Olefin Methatesis and Methatesis Polymerization*. Academic Press: London, 1997.
16.	Amini, M.; Haghdoost, M. M.; Bagherzadeh, M., *Coord. Chem. Rev.* **2013,** *257*, 1093.
17.	Stiefel, E., *Proc. Nat. Acad. Sci. USA* **1973,** *70*, 988.
18.	Gatehouse, B. M.; Leverett, P., *J. Chem. Soc. A* **1969**, 849.
19.	Hove, A. R.; Bildsøe, H.; Skibsted, J.; Brorson, M.; Jakobsen, H. J., *Inorg. Chem.* **2006,** *45*, 10873.
20.	Cruywagen, J. J., *Adv. Inorg. Chem.* **2000,** *49*, 127.
21.	Busey, R. H.; Keller, O. L. J., *J. Chem. Phys.* **1964,** *41*, 715.
22.	Vold, R. R.; Vold, R. L., *J. Magn. Reson.* **1975,** *19*, 365.
23.	Pope, T. M., *Heteropoly and Isopoly Oxometalates*. Springer-Verlach: Berlin, 1983.
24.	Howarth, O. W.; Kelly, P. J., *J. Chem. Soc., Dalton Trans.* **1990**, 81.
25.	Cruywagen, J. J., *Inorg. Chem.* **1980,** *19*, 552.
26.	Wilkinson, S. G., *Comprehensive Coordination Chemistry*. Pergamon Press: 1987; Vol. 3.
27.	Himeno, S.; Ueda, Y.; Hasegawa, M., *Inorg. Chim. Acta* **1983,** *70*, 53.
28.	Himeno, S.; Hasegawa, M., *Inorg. Chim. Acta* **1983,** *73*, 255.
29.	Cruywagen, J. J.; Heyns, J. B. B.; Rohwer, E. F. C. H., *J. Inorg. Nucl. Chem.* **1976,** *38*, 2033.
30.	Aveston, J.; Anacher, E. W.; Johnson, J. S., *Inorg. Chem.* **1964,** *3*, 755.
31.	Rosenheim, A., *Z. Anorg. Allg. Chem.* **1906,** *50*, 320.
32.	Heyns, J. B. B.; Cruywagen, J. J., *Inorg. Synth.* **1986,** *24*, 191.
33.	Schumb, W. C.; Hartford, W. H., *J. Am. Chem. Soc.* **1934,** *56*, 2613.
34.	Hornebecq, V.; Mastai, Y.; Antonietti, M., *Chem. Mater.* **2003,** *15*, 3586.
35.	Calin, N.; Sevrov, S. C., *Inorg. Chem.* **2003,** *42*, 7304.
36.	Stiefel, E. I., *Prog. Inorg. Chem.* **1977,** *22*, 1.
37.	Albright, T. A.; Burdett, J. K.; Whaugbo, M. H., *Orbital Interactions in Chemistry*. John Wiley & Sons: New York, 1985.
38.	Griffith, W. P.; Wickins, T. D., *J. Chem. Soc. A* **1968**, 400.
39.	Cotton, F. A.; Wing, R. M., *Inorg. Chem.* **1965,** *4*, 867.
40.	Cotton, F. A.; Morehouse, S. M.; Wood, J. S., *Inorg. Chem.* **1964,** *3*, 1603.
41.	Spivack, B.; Dori, Z., *Coord. Chem. Rev.* **1975,** *17*, 99.
42.	Appleton, T. G.; Clark, H. C.; Manzer, L. E., *Coord. Chem. Rev.* **1973,** *10*, 335.
43.	Burdett, J. K.; Albright, T. A., *Inorg. Chem.* **1979,** *18*, 2112.

44. Shustorovich, E. M.; Porai-Koshits, M. A.; Buslaev, Y. A., *Coord. Chem. Rev.* **1975,** *17*, 1.

45. Holm, R. H., *Chem. Rev.* **1987,** *87*, 1401.

46. Dienann, E.; Muller, A., *Coord. Chem. Rev.* **1972,** *10*, 79.

47. Kula, R. J., *Anal. Chem.* **1966,** *38*, 1382.

48. McCleverty, J. A.; Meyer, T. J., *Comprehensive Coordination Chemistry II*. Pergamon: 2003; Vol. 4.

49. Butcher, R. J.; Penfold, B. R.; Sinn, E., *J. Chem. Soc., Dalton Trans.* **1979**, 668.

50. Dietrich, A.; Neumuller, B.; Dehnicke, K., *Z. Anorg. Allg. Chem.* **1999,** *625*, 1321.

51. Hursthouse, M. B.; Motevalli, M., *J. Chem. Soc., Dalton Trans.* **1979**, 1362.

52. Bishop, M. W.; Chatt, J.; Dilworth, J. R.; Hursthouse, M. B.; Montevalle, M., *J. Less. Common Met.* **1977,** *54*, 487.

53. Dickman, M. H.; Pope, M. T., *Chem. Rev.* **1994,** *94*, 569.

54. Edwards, A. J.; Steventon, B. R., *J. Chem. Soc. A* **1968**, 2503.

55. Taylor, J. C.; Waugh, A. B., *Journal of the Chemical Society, Dalton Transactions* **1980**, 2006.

56. Dreisch, K.; Andersson, C.; Haakansson, M.; Jagner, S., *J. Chem. Soc., Dalton Trans.* **1993**, 1045.

57. Rhiel, M.; Wacadlo, S.; Massa, W.; Dehnicke, K., *Z. Anorg. Allg. Chem.* **1996,** *622*, 1195.

58. Drake, J. E.; Hursthouse, M. B.; Light, M. E.; Kumar, R.; Ratnani, R., *Journal of Chemical Crystallography* **2007,** *37*, 421.

59. Huch, V.; Kumar, R.; Mathur, R.; Ratnani, R., *J. Chem. Crystallogr.* **2008,** *38*, 605.

60. Nugent, W. A.; Mayer, J. M., *Metal-ligand multiple bonds*. Wiley: New York, 1988.

61. Barea, G.; Lledos, A.; Maseras, F.; Jean, Y., *Inorg. Chem.* **1998,** *37*, 3321.

62. Berg, J. M.; Hogson, K. O., *Inorg. Chem.* **1980,** *19*, 2180.

63. Buchanan, T.; Minelli, M.; Ashby, M. T.; King, T. J.; Enemark, J. H.; Garner, C. D., *Inorg. Chem.* **1984,** *23*, 495.

64. Ramana Rao, D. V., *Anal. Chim. Acta* **1957,** *17*, 538.

65. Gehrke Jr, H.; Veal, J., *Inorganica Chimica Acta* **1969,** *3*, 623.

66. Cotton, F. A.; Elder, R. C., *Inorg. Chem.* **1964,** *3*, 397.

67. Zhou, Z. H.; Wan, H. L.; Tsai, K. R., *Inorg. Chem.* **2000,** *39*, 59.

68. Herrmann, W.; Wieghardt, K., *Polyhedron* **1986,** *5*, 513.

69. Wieghardt, K.; Hahn, M.; Swiridoff, W.; Weiss, J., *Inorg. Chem.* **1984,** *23*, 94.

70. Park, J. J.; Glick, M. D.; Hoard, J. L., *J. Am. Chem. Soc.* **1969,** *91*, 301.

71. Patterson, L., *Acta Chem. Scand.* **1972,** *26*, 4067.

72. Cindric, M.; Strukan, N.; Vrdoljak, V.; Devcic, M.; Veksli, Z.; Kamenar, B., *Inorg. Chim. Acta* **2000,** *304*, 260.

73. Matsumoto, K.; Marutani, Y.; Ooi, S.-I., *Bull. Chem. Soc. Jpn.* **1984,** *57*, 2671.

74. Chen, Q.; Liu, S.; Zubieta, J., *Inorg. Chim. Acta* **1989,** *162*, 163.

75. Werndrup, P.; Seisenbaeva, G. A.; Westin, G.; Persson, I.; Kessler, V. G., *Eur. J. Inorg. Chem.* **2006**, 1413.

76. Ellsworth, J. M.; Smith, M. D.; Zur Loye, H.-C., *Solid State Sci.* **2008,** *10*, 1822.

77. An, H.; Xu, T.; Jia, C.; Zheng, H.; Mu, W., *J. Mol. Struct.* **2009,** *933*, 86.

78. Nelson, D. L.; Cox, M. M., *Lehninger Principles of Biochemistry*. 5 ed.; W. H. Freeman and Company: 2004.

79. Shaw, W. J., *Catalysis Reviews-Science and Engineering* **2012,** *54*, 489.

80. Desbouis, D.; Troitsky, I. P.; Belousoff, M. J.; Spiccia, L.; Graham, B., *Coordination Chemistry Reviews* **2012,** *256*, 897.

81. Micskei, K.; Patonay, T.; Caglioti, L.; Palyi, G., *Chemistry & Biodiversity* **2010,** *7*, 1660.

82. Severin, K.; Bergs, R.; Beck, W., *Angew. Chem.-Int. Edit.* **1998,** *37*, 1635.

83. Djordjevic, C.; Vuletic, N.; Sinn, E., *Inorg. Chim. Acta* **1985,** *104*, L7.

84. Djordjevic, C.; Vuletic, N.; Jacobs, B. A.; LeeRenslo, M.; Sinn, E., *Inorg. Chem.* **1997,** *36*, 1798.

85. Sastry, M. S.; Gupta, S. S., *Transition Met. Chem.* **1996,** *21*, 410.

86. Zhu, W. S.; Li, H.; Gu, Q. Q.; Wu, P.; Zhu, G.; Yan, Y.; Chen, G., *J. Mol. Catal. A: Chem.* **2011,** *336*, 16.

87. Tarafder, M. T. H.; Khan, A. R., *Indian J. Chem. A* **1993,** *32*, 781.

88. Serdiuk, K.; Gancarz, R.; Cieslak-Golonka, M., *Transition Met. Chem.* **2001,** *26*, 538.

89. Sastry, M. S.; Gupta, S. S., *Proc. Indian Acad. Sci.* **1997,** *109*, 173.

90. Kapoor, S.; Sastry, M. S., *Int. J. Chem. Kinet.* **1999,** *31*, 159.

91. Kamenar, B.; Korpar-Colig, B.; Penavic, M.; Cindric, M., *J. Chem. Soc., Dalton Trans.* **1990**, 1125.

92. Inoue, M.; Yamase, T., *Bull. Chem. Soc. Jpn.* **1995,** *68*, 3055.

93. Lu, J. J.; Xu, Y., *Chem. Mater.* **1998,** *10*, 4141.

94. Liu, G.; Wei, Y. G.; Liu, J.; Liu, Q.; Zhang, S. W.; Tang, Y. Q., *J. Chem. Soc., Dalton Trans.* **2000**, 1013.

95. Liu, G.; Zhang, S. W.; Tang, Y. Q., *Z. Anorg. Allg. Chem.* **2001,** *627*, 1077.

96. Liu, G.; Zhang, S. W., *Acta Cryst. C* **2002,** *58*, m92.

97. Wu, X. Y.; Liu, J. H.; Zhang, Q. Z.; He, X.; Chen, S. M.; Lu, C. Z., *Acta Cryst. E* **2004,** *60*, M921.

98. Cindric, M.; Novak, T. K.; Kraljevic, S.; Kralj, M.; Kamenar, B., *Inorg. Chim. Acta* **2006,** *359*, 1673.

99. Cartuyvels, E.; Van Hecke, K.; Van Meervelt, L.; Gorller-Walrand, C.; Parac-Vogt, T. N., *J. Inorg. Biochem.* **2008,** *102*, 1589.

100. Shi, Y.; Ren, X.; Ren, S.; Fu, F.; Wang, J.; Xue, G., *J. Chem. Crystallogr.* **2010,** *40*, 985.

101. Cindric, M.; Strukan, N.; Devcic, M.; Kamenar, B., *Inorg. Chem. Comm.* **1999,** *2*, 558.

102. Kortz, U.; Savelieff, M. G.; Ghali, F. Y. A.; Khalil, L. M.; Maalouf, S. A.; Sinno, D. I., *Angew. Chem. Int. Ed.* **2002,** *41*, 4070.

103. Kortz, U.; Vaissermann, J.; Thouvenot, R.; Gouzerh, P., *Inorg. Chem.* **2003,** *42*, 1135.

104. Li, J.; Xu, L.; Jiang, N.; Zhao, L.; Li, F., *Struct. Chem.* **2011,** *22*, 1339.

105. Spence, J. T.; Chang, H. Y., *Inorg. Chem.* **1963,** *2*, 319.

106. Spence, J. T.; Lee, J. Y., *Inorg. Chem.* **1965,** *4*, 385.

107. Martin, J. F.; Spence, J. T., *J. Phys. Chem.* **1970,** *74*, 2863.

108. Brown, D. H.; Macphers, J., *J. Inorg. Nucl. Chem.* **1972,** *34*, 1705.

109. Cavaleiro, A.; Dejesus, J. D. P.; Gil, V. M. S.; Gillard, R. D.; Williams, P. A., *Transition Met. Chem.* **1982,** *7*, 75.

110. Martire, D. O.; Feliz, M. R.; Capparelli, A. L., *Polyhedron* **1989,** *8*, 2225.

111. Domenech, A.; Llopis, E.; Garciaespana, E.; Cervilla, A., *Transition Met. Chem.* **1990,** *15*, 425.

112. Cruywagen, J. J.; Heyns, J. B. B.; Rohwer, E. A., *J. Chem. Soc., Dalton Trans.* **1993**, 1713.

113. Gharib, F.; Zare, K.; Khorrami, S. A.; Behju, A., *J. Chem. Eng. Data* **1995,** *40*, 1214.

114. Gharib, F.; Khorrami, S. A.; Sharifi, S., *Proc. Indian Acad. Sci.* **1997,** *109*, 71.

115. Gharib, F.; Zare, K.; Majlesi, K., *J. Chem. Eng. Data* **2000,** *45*, 833.

116. Gharib, F.; Zare, K.; Taghvamanesh, A.; Monajjemi, M., *J. Chem. Eng. Data* **2001,** *46*, 1140.

117. Gharib, F.; Malekani, M., *Rev. Inorg. Chem.* **2003,** *23*, 97.

118. Monajjemi, M.; Azizi, Z.; Ghavami, M., *Russ. J. Inorg. Chem.* **2003,** *48*, 1551.

119. Majlesi, K.; Zare, K., *Russ. J. Inorg. Chem.* **2005,** *50*, 1621.

120. Monajjemi, M.; Azizi, Z.; Moniri, E., *Russ. J. Inorg. Chem.* **2005,** *79*, 1209.

121. Majlesi, K.; Zare, K., *Phys. Chem. Liq.* **2006,** *44*, 257.

122. Majlesi, K.; Zare, K., *J. Mol. Liq.* **2006,** *125*, 66.

123. Gharib, F.; Jabbari, M.; Farajtabar, A.; Shamel, A., *J. Chem. Eng. Data* **2008,** *53*, 1772.

124. Rabenstein, D. L.; Greenberg, M. S.; Saetre, R., *Inorg. Chem.* **1977,** *16*, 1241.

125. Shen, Z.; Xu, H.; Chen, Z., *Acta Phys.-Chim. Sin.* **1987,** *3*, 265.

126. Cavaleiro, A. M. V. S. V.; Dejesus, J. D. P.; Gil, V. M. S.; Gillard, R. D.; Williams, P. A., *Inorg. Chim. Acta* **1990,** *172*, 25.

127. Callis, G. E.; Wentworth, R. A. D., *Bioinorg. Chem.* **1977,** *7*, 57.

128. Freeman, M. A.; Schultz, F. A.; Reilley, C. N., *Inorg. Chem.* **1982,** *21*, 567.

129. Singh, M. K.; Srivasta.Mn, *J. Inorg. Nucl. Chem.* **1972,** *34*, 2081.

130. Tewari, R. C.; M., S., *Talanta* **1973,** *20*, 133.

131. Johansen, E. S.; Jons, O., *Acta Chem. Scand.* **1981,** *35*, 233.

132. Butcher, R. J.; Powell, H. K. J.; Wilkins, C. J.; Yong, S. H., *J. Chem. Soc., Dalton Trans.* **1976**, 356.

133. Kay, A.; Mitchell, P. C., *J. Chem. Soc. A* **1970,** *14*, 2421.

134. Takeuchi, H. E. T.; Furuhashi, A. O. A., *Bull. Chem. Soc. Jpn.* **1969,** *42*, 3585.

135. Nagaraja, K. S.; Udupa, M. R., *Indian J. Chem. A* **1983,** *22*, 531.

136. Castillo, M.; Palma, P., *Synth. React. Inorg. Met.-Org. Chem.* **1984,** *14*, 1173.

137. Vassilev, K.; Dimitrova, M.; Turmanova, S.; Milina, R., *Synth. React. Inorg. Met.-Org. Chem.* **2013,** *43*, 243.

138. Conte, V.; Di Furia, F.; Licini, G., *Appl. Cat. A : General* **1997,** *157*, 335.

139. Van Santen, R.; Kuipers, H. P. C. E., *Adv. Catal.* **1987,** *35*, 256.

140. Van Santen, R., *Handbook of Heterogeneous catalysis*. John Wiley & Son: Weinheim, 1997; Vol. 5.

141. Leinomen, S.; Sherrington, D. C.; Sneddon, A.; McLoughlin, D.; Corker, J.; Canevali, C.; Morazzoni, F.; Reedijk, J.; Spratt, S. B. D., *J. Catal.* **1999,** *183*, 251.

142. Swern, D., *Organic Peroxides*. John Wiley & Son: New York, 1971; Vol. 2.

143. Gago, S.; Balula, S. S.; Figueiredo, S.; Lopes, A. D.; Valente, A. A.; Pillinger, M.; Gocalves, I. S., *Appl. Cat. A : General* **2010,** *372*, 67.

144. Riisio, A.; Lehtonen, A.; Hanninen, M. M.; Sillanpaa, R., *Eur. J. Inorg. Chem.* **2013**, 1499.

145. Gomez, M.; Jansat, S.; Muller, G.; Noguera, G.; Terudel, H.; Moliner, V.; Cerrada, E.; Hursthouse, M., *Eur. J. Inorg. Chem.* **2001**, 1071.

146. Wong, Y.-L.; Ng, D. K. P.; Lee, Y. K., *Inorg. Chem.* **2002,** *41*, 20.

147. Punniyamurthy, T.; Velusamy, S.; Iqbal, J., *Chem. Rev.* **2005,** *105*, 2329.

148. Conte, V.; Bortolini, O., *Chemistry of Peroxides*. Z. Rappoport ed.; 2006; Vol. 2 : Transition metal peroxides, Synthesis and role in oxidation reactions.

149. Sharpless, K. B.; Townsend, J. M.; Williams, D. R., *J. Am. Chem. Soc.* **1972,** *94*, 295.

150. Brégeault, J.-M., *J. Chem. Soc., Dalton Trans.* **2003**, 3289.

151. Trost, M. K.; Bergman, R. G., *Organomet.* **1991,** *10*, 1172.

152. Ambroziak, K.; Pelech, R.; Milchert, E.; Dziembowska, T.; Rozwadowski, Z., *J. Mol. Catal. A: Chem.* **2004,** *211*, 9.

153. Gnecco, J. A.; Borda, G.; Reyes, P., *J. Chil. Chem. Soc.* **2004,** *49*, 179.

154. Kotov, S. V.; Georgieva, M. G.; Kolev, T. M., *J. Mol. Catal. A: Chem.* **2004,** *207*, 5.

155. Wang, G.; Chen, G.; Luck, R. L.; Wang, Z.; Mu, Z.; Evans, D. G.; Duan, X., *Inorg. Chim. Acta* **2004,** *357*, 3223.

156. Petrovski, Z.; Pillinger, M.; Valente, A. A.; Goncalves, I. S.; Hazell, A.; Romao, C. C., *J. Mol. Catal. A: Chem.* **2005,** *227*, 67.

157. Topuzovaa, M. G.; Kotov, S. V.; Kolev, T. M., *Appl. Cat. A : General* **2005,** *281*, 157.

158. Elisabete da Palma Carreiro, A. J. B., *J. Mol. Catal. A: Chem.* **2006,** *249*, 123.

159. Salavati-Niasari, M.; Bazarganipour, M., *J. Mol. Catal. A: Chem.* **2007,** *278*, 173.

160. Abdel Aziz, A. A., *J. Mol. Struct.* **2010,** *979*, 77.

161. Dimitrova, M.; Turmanova, S.; Vassilev, K., *Reac. Kinet. Mech. Cat.* **2010,** *99*, 69.

162. Rezaeifard, A.; Sheikhshoaie, I.; Monadi, N.; H., S.-E., *Eur. J. Inorg. Chem.* **2010**, 799.

163. Bagherzadeha, B. Z., M.; Amani, V.; Ellern, A.; Woo, L. K., *Polyhedron* **2013,** *53*, 223.

164. Chandra, P.; Pandhare, S. L.; Umbarkar, S. B.; Dongare, M. K.; Vanka, K., *Chem. Eur. J.* **2013,** *19*, 2030.

165. Tangestaninejad, S.; Moghadam, M.; Mirkhani, V.; Mohammadpoor-Baltork, I.; Ghani, K., *Inorg. Chem. Commun.* **2008,** *11*, 270.

166. Salavati-Niasari, M.; Bazarganipour, M., *Transition Met. Chem.* **2008,** *33*, 751.

167. Carrasco, C. J.; Montilla, F.; Alvarez, E.; Herbert, M.; Galindo, A., *Polyhedron* **2013,** *54*, 123.

168. Csanyi, L. J.; Jaki, K., *J. Catal.* **1991,** *127*, 42.

169. Gharah, N.; Chattopadhyay, B.; Maiti, S. K.; Mukherjee, M., *Transition Met. Chem.* **2010,** *35*, 531.

170. Talsi, E. P.; Shalyaev, K. V.; Zamaraev, K. I., *J. Mol. Catal.* **1993,** *83*, 347.

171. Maurya, M. R.; Arya, A.; Adao, P.; Costa Pessoa, J., *Appl. Cat. A : General* **2008,** *351*, 239.

172. Cao, L.; Yang, M.; Wang, G.; Wei, Y.; Sun, D., *J. Polym. Sci., Part A* **2009,** *48*, 558.

173. Biradar, A. V.; Sathe, B. R.; Umbarkar, S. B.; Dongare, M. K., *J. Mol. Catal. A: Chem.* **2008,** *285*, 111.

174. Afsharpour, M.; Mahjoub, A. R.; Amini, M. M., *Appl. Cat. A : General* **2007,** *327*, 205.

175. Sheldon, R. A.; Arends, I. W. C. E.; Hanefeld, U., *Green Chemistry and Catalysis*. Wiley-VCH: Weinheim, 2007.

176. Strukul, G., *Catalytic Oxidation with Hydrogen Peroxide as Oxidant*. Kluwer Academic Publisher: 1992.

177. Jolly, W. J., *Synthetic Inorganic Chemistry*. Prentice-Hall, Inc.: 1960.

178. Dittmann, M.; Schweda, E., *Z. Anorg. Allg. Chem.* **1998,** *624*, 2033.

179. Wu, X. L.; Burns, S. T.; Zilm, K. W., *Journal of Magnetic Resonance, Series A* **1994,** *111*, 29.

180. Hu, J. Z.; Harper, J. K.; Taylor, C.; Pugmire, R. J.; Grant, D. M., *Journal of Magnetic Resonance* **2000,** *142*, 326.

181. Crouthamel, C. E.; Johnson, C. E., *Anal. Chem.* **1954,** *26*, 1284.

182. Eckhardt, R.; Eggers, D.; Slutsky, L. J., *Spectrochim. Acta* **1970,** *26A*, 2033.

183. Harris, D. H., *Quantitative Chemical Analysis*. 7nd ed.; W. H. Freeman and company: New York, 1997.

184. Gottlieb, H. E.; Kotlyar, V.; Nudelman, A., *J. Org. Chem.* **1997,** *62*, 7512.

185. Stephenson, N. A.; Bell, A. T., *Anal. Bioanal. Chem.* **2005,** *381*, 1289.

186. Yamaji, T. H., K.; Yanagisawa, K. M.; Yamamoto, O.; Wasada, N.; Someno, K.; Kinugasa, S.; Tanabe, K.; Tamura, T.; Hiraishi, J.; Saito, T. T., *Spectral Database for Organic Compounds*, http://sdbs.db.aist.go.jp/sdbs/cgi-bin/cre_index.cgi.

187. Duffy, E. M.; Jorgensen, W. L., *J. Am. Chem. Soc.* **2000,** *122*, 2878.

188. Sangster, J., *J. Phys. Chem. Ref. Data* **1989,** *18*, 1111.

189. Scanlon, J. T.; Willis, D. E., *J. Chromatogr. Sci.* **1985,** *23*, 333.

190. Sigma-Aldrich, *http://www.sigmaaldrich.com*.

191. Papenguth, H. W.; Kirkpatrick, R. J.; Montez, B.; Sandberg, P. A., *Am. Mineral.* **1989,** *74*, 1152.

192. Cotton, F. A.; Jackman, L. M., *Dynamic Nuclear Magnetic Resonance Spectroscopy*. Elsevier: 1975.

193. Müller, A.; Meyer, J.; Krickemeyer, E.; Diemann, E., *Angew. Chem. Int. Ed.* **1996,** *35*, 1206.

194. McNaught, A. D.; Wilkinson, A., *Compendium of Chemical Terminology - the "Gold Book"*. 2nd ed.; IUPAC: Oxford, 1997.

195. Hays, G. R., *J. Chem. Soc., Perkin Trans.* **1983**, 1049.

196. Duer, M. J., *Solid State NMR Spectroscopy: Principles and Applications*. 2002.

197. Batchelor, J. G.; Feeney, J.; Roberts, G. C. K., *J. Magn. Reson.* **1975,** *20*, 19.

198. Quirt, A. R.; Lyerla, J. R., Jr.; Peat, I. R.; Cohen, J. S.; Reynolds, W. F.; Freedman, M. H., *J. Am. Chem. Soc.* **1974,** *96*, 570.

199. Surprenant, H. L.; Sarneski, J. E.; Key, R. R.; Byrd, J. T.; Reilley, C. N., *J. Magn. Reson.* **1980,** *40*, 231.

200. Christl, M.; Roberts, J. D., *J. Am. Chem. Soc.* **1972,** *94*, 4565.

201. Gurd, F. R.; Lawson, P. J.; Cochran, D. W.; Wenkert, E., *J. Biol. Chem.* **1971,** *246*, 3725.

202. Jung, G.; Ottnad, M.; Voelter, W.; Breitmaier, E., *Fresen. J. Anal. Chem.* **1972,** *261*, 328.

203. Pople, J. A.; Schneider, W. G.; Bernstein, H. J., *High-resolution Nuclear Magnetic Resonance*. McGraw-Hill: New York, 1959.

204. Cambridge Crystallographic Data Centre, *http://www.ccdc.cam.ac.uk/pages/Home.aspx*

205. Narayanan, P.; Venkataraman, S., *J. Cryst. Mol. Struct.* **1975,** *5*, 15.

206. Sridhar, B.; Srinivasan, N.; Rajaram, R. K., *Acta Cryst. E* **2002,** *58*, o1103.

207. Pandiarajan, S.; Sridhar, B.; Rajaram, R. K., *Acta Cryst. E* **2002,** *58*, o862.

208. Asath Bahadur, S.; Rajaram, R. K.; Nethaji, M.; Natarajan, S., *Z. Kristallogr.* **2010,** *203*, 93.

209. Berrah, F.; Benali-Cherif, N.; Lamraoui, H., *Acta Cryst. E* **2005,** *61*, o1517.

210. Pandiarajan, S.; Sridhar, B.; Rajaram, R. K., *Acta Cryst. E* **2002,** *58*, o862.

211. Srikrishnan, T.; Narasinga Rao, S.; Parthasarathy, R., *Acta Cryst. A* **1984,** *40*, C92.

212. Gorbitz, C. H., *Acta Cryst. E* **2001,** *57*.

213. Marsh, R. E., *Acta Cryst.* **1958,** *11*.

214. Torii, K.; Iitaka, Y., *Acta Cryst.* **1973,** *B29*.

215. Gorbitz, C. H.; Dalhus, B., *Acta Cryst. C* **1996,** *C52*, 1754.

216. Muller, G.; Maier, G. M.; Lutz, M., *Inorg. Chim. Acta* **1994,** *218*, 121.

217. Max, J. J.; Chapados, C., *J. Phys. Chem. A* **2004,** *108*, 3324.

218. Rosadoa, M. T.; Duarte, M. L. T. S.; Fausto, R., *Vib. Spectrosc.* **1998,** *16*, 35.

219. McAuliffe, C. A.; Quagliano, J. V.; Vallarino, L. M., *Inorg. Chem.* **1966,** *5*, 1996.

220. Gervais, C.; Dupree, R.; Pike, K. J.; Bonhomme, C.; Profeta, M.; Pickard, C. J.; Mauri, F., *J. Phys. Chem. A*

2005, *109*, 6960.

221.   Ye, B. H.; Li, X. Y.; Williams, I. D.; Chen, X. M., *Inorg. Chem.* **2002,** *41*, 6426.

222.   Lin, S.; Hong, T. N.; Tung, J. Y.; Chen, J. H. R., *Inorg. Chem.* **1997,** *36*, 3886.

223.   Tsuboi, M.; Onishi, T.; Nakagawa, T. S.; Mizushima, S. I., *Spectrochim. Acta* **1958,** *12*, 253.

224.   Olsztynska, S.; Komorowska, M.; Vrielynck, L.; Dupuy, N., *Appl. Spectrosc.* **2001,** *55*, 901.

225.   Jackovitz, J. F.; Walter, J. L., *Spectrochim. Acta* **1966,** *22*, 1393.

226.   Grunenberg, A.; Bougeard, D., *J. Mol. Struct.* **1987,** *160*, 27.

227.   Wagner, C. C.; Torre, M. H.; Baran, E. J., *Lat. Am. J. Pharm.* **2008,** *27*, 197.

228.   Griffith, W. P., *J. Chem. Soc. A* **1969**, 211.

229.   Cousins, M.; Green, M. L. H., *J. Chem. Soc. (Resumed)* **1964**, 1567.

230.   Larson, M. L.; Moore, F. W., *Paper submitted to the 149th meeting of the American Chemical Society* **1965**.

231.   Coddington, J. M.; Taylor, M. J., *J. Chem. Soc., Dalton Trans.* **1990**, 41.

232.   Taylor, J. M.; Clifton, E. F. R.; Lars, A. K., *J. Chem. Soc., Dalton Trans.* **1998**, 3195.

233.   Florian, L. R.; Corey, E. R., *Inorg. Chem.* **1968,** *7*, 722.

234.   Fenn, R. H., *J. Chem. Soc. A* **1969**, 1764.

235.   Magee, R. J.; Witwit, A. S., *Anal. Chim. Acta* **1963,** *29*, 517.

236.   Atovmyan, L. O.; Sokolova, Y. A., *Zh. Struk. Khim.* **1971,** *12*, 851.

237.   Moore, F. W.; Rice, R. E., *Inorg. Chem.* **1968,** *7*, 2510.

238.   Craven, B. M.; Ramey, K. C.; Wise, W. B., *Inorg. Chem.* **1971,** *10*, 2626.

239.   Kamenar, B.; Penavic, B. M.; Prout, C. K., *Cryst. Struct. Commun.* **1973,** *2*, 41.

240.   Kojic-Prodic, B.; Ruzic-Toros, Z.; Grdenic, D.; Golic, L., *Acta Cryst. B* **1974,** *30*, 300.

241.   Sawyer, D. T.; McKinnie, J. M., *J. Am. Chem. Soc.* **1960,** *82*, 4191.

242.   Clark, G. M.; Doyle, W. P., *Spectrochim. Acta* **1966,** *22*, 1441.

243.   Sabat, H.; Rudolf, M. F.; Jezowska-Trzebiatowska, B., *Inorg. Chim. Acta* **1973,** *7*, 365.

244.   Griffith, W. P.; Hewkin, D. J., *J. Chem. Soc.* **1966**, 472.

245.   Wing, R. M.; Callahan, K. P., *Inorg. Chem.* **1969,** *8*, 871.

246.   Rheingold, A. L.; Harper, J. R., *J. Organomet. Chem.* **1991,** *403*, 335.

247.   Partyka, D. V.; Staples, R. J.; Holm, R. H., *Inorg. Chem.* **2003,** *42*, 7877.

248.   Cindric, M.; Strukan, N.; Kajfez, T.; Giester, G.; Kamenar, B., *Inorg. Chem. Comm.* **2000,** *3*, 281.

249.   Zhang, J.; Guo, Y.; Lu, W.; Guo, X.; Xu, M.; Guo, H., *J. Ind. Eng. Chem.* **2012,** *18*, 1824.

250.   Lin, B.-Z.; Liu, P.-D., *J. Mol. Struct.* **2003,** *654*, 55.

251.   Coelho, A. C.; Nolasco, M.; Balula, S. S.; Antunes, M. M.; Pereira, C. C. L.; Almeida Paz, F. A.; Valente, A. A.; Pillinger, M.; Ribeiro-Claro, P.; Klinowski, J.; Gonçalves, I. S., *Inorg. Chem.* **2010,** *50*, 525.

252.   Cindric, M.; Vrdoljak, V.; Strukan, N.; Kamenar, B., *Polyhedron* **2005,** *24*, 369.

253.   Wieghardt, K.; Holzbach, W.; Weiss, J., *Inorg. Chem.* **1981,** *20*, 3436.

254.   Kim, N.; Kim, S.; Vella, P. A.; Zubieta, J., *Inorg. Nucl. Chem. Lett.* **1978,** *14*, 457.

255.   Sobczak, J. M.; Glowiak, T.; Ziolkowski, J. J., *Transition Met. Chem.* **1990,** *15*, 208.

256.   Lehtonen, A.; Sillanpaa, R., *Polyhedron* **2005,** *24*, 257.

257.   Cotton, F. A.; Morehouse, S. M., *Inorg. Chem.* **1965,** *4*, 1377.

258.   Cindric, M.; Strukan, N.; Vrdoljak, V.; Kajfez, T.; Kamenar, B., *Z. Anorg. Allg. Chem.* **2002,** *628*, 2113.

259.   Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. 4 ed.; John Wiley & Sons: 1986.

260.   Nakamoto, K.; Fujita, J.; Tanaka, S.; Kobayashi, M., *J. Am. Chem. Soc.* **1957,** *79*, 4904.

261.   Deacon, G. B.; Phillips, R. J., *Coord. Chem. Rev.* **1980,** *33*.

262.   Robinson, S. D.; Uttley, M. F., *J. Chem. Soc., Dalton Trans.* **1973**, 1912.

263.   Nara, M.; Torii, H.; Tasumi, M., *J. Phys. Chem.* **1996,** *100*, 19812.

264.   Ito, K. B.; Bernstein, H. J., *Can. J. Chem.* **1956,** *34*, 170.

265.   Zhou, Z. H.; Hou, S. Y.; Cao, Z. X.; Wan, H. L.; Ng, S. W., *J. Inorg. Biochem.* **2004,** *98*, 1037.

266.   Modec, B.; Dolenc, D.; Kasunic, M., *Inorg. Chem.* **2008,** *47*, 3625.

267.   Cindric, M.; Novak, T. K.; Kraljevic, S.; Kralj, M.; Kamenar, B., *Inorg. Chim. Acta* **2006,** *359*, 1673.

268. Cartuyvels, E.; Van Hecke, K.; Van Meervelt, L.; Gorller-Walrand, C.; Parac-Vogt, T. N., *J. Inorg. Biochem.* **2008,** *102*, 1589.

269. Zhou, Z. H.; Zhao, H.; Tsai, K. R., *J. Inorg. Biochem.* **2004,** *98*, 1787.

270. Edwards, C. F.; Griffith, W. P.; White, A. J. P.; Williams, D. J., *J. Chem. Soc., Dalton Trans.* **1993**, 3813.

271. Chesalov, Y. A.; Chernobai, G. B.; Boldyreva, E. V., *J. Struct. Chem.* **2008,** *49*, 1012.

272. Korpar-Colig, B.; Cindric, M.; Matkovic-Calogovic, D.; Vrdoljak, V.; Kamenar, B., *Polyhedron* **2002,** *21*, 147.

273. Maiti, S. K.; Malik, K. M. A.; Gupta, S.; Chakraborty, S.; Ganguli, A. K.; Mukherjee, A. K.; Bhattacharyya, R., *Inorg. Chem.* **2006,** *45*, 9843.

274. Chen, S. M.; Lu, C. Z.; Yu, Y. Q.; Zhang, Q. Z.; He, X., *Acta Cryst. C* **2004,** *60*, m437.

275. Shimanouchi, T., *Table of molecular vibrational frequencies*. U.S. National Standards Reference Data System: 1972; Vol. 1.

276. Livingstone, S. E.; Nolan, J. D., *Inorg. Chem.* **1968,** *7*, 1447.

277. Melly, L. R., *Inorg. Chem.* **1969,** *8*, 349.

278. Stone, P. J.; Craig, J. C.; Thompson, H. W., *J. Chem. Soc. (Resumed)* **1958**, 52.

279. Heacock, R. A.; Marion, L., *Can. J. Chem.* **1956,** *34*, 1782.

280. Watson, C. C., *Spectrochim. Acta* **1960,** *16*, 1322.

281. Koleva, B. B., *Vib. Spectrosc.* **2007,** *44*, 30.

282. Hayatifar, M.; Marchetti, F.; Pampaloni, G.; Zacchini, S., *Inorg. Chem.* **2013**, 4017.

283. Knobler, C.; Penfold, B. R.; Robinson, W. T.; Wilkins, C. J.; Yong, S. H., *J. Chem. Soc., Dalton Trans.* **1980**, 248.

284. Yamase, T.; Inoue, M.; Naruke, H.; Fukaya, K., *Chem. Lett.* **1999,** *7*, 563.

285. Berkowitz, J.; Inghram, M. G.; Chupka, W. A., *J. Chem. Phys.* **1957,** *26*, 842.

286. Brisdon, A. K., *Inorganic Spectroscopic Methods*. Oxford UP: Oxford, 1998.

287. Huheey, J. E.; Keiter, E. A.; Keiter, R. L., *Inorganic Chemistry: Principles of Structure and Reactivity*. HarperCollins College: New York, 1993

288. So, H.; Pope, M. T., *Inorg. Chem.* **1972,** *11*, 1441.

289. Sacht, C.; Datt, M. S., *Polyhedron* **2000,** *19*, 1347.

290. Calligaris, M., *Coord. Chem. Rev.* **2004,** *248*, 351.

291. Gaylord Chemical Company, L. L. C. *Technical Bulletin Reaction Solvent Dimethyl Sulfoxide (DMSO)*.

292. Rozhko, E.; Raabova, K.; Macchia, F.; Malmusi, A.; Righi, P.; Accorinti, P.; Alini, S.; Babini, P.; Cerrato, G.; Manzoli, M.; Cavani, F., *ChemCatChem* **2013,** *5*, 1998.

293. Masson, O., *J. Chem. Soc., Trans.* **1907,** *91*, 1449.

294. Sheridan, R. C.; Brown, E. H., *J. Org. Chem.* **1965,** *30*, 668.

295. Brazdil, J. F.; Glaeser, L. C.; Teller, R. G. *Conversion of acetonitrile to glycolonitrile and/or glycolamide.* US4634789 A, 1987.

296. Wolfsie, J. H., *J. Occup. Environ. Med.* **1960,** *2*, 588.

297. Yin, C.; Yang, Z.; Li, B.; Zhang, F.; Wang, J.; Ou, E., *Catal. Lett.* **2009,** *131*, 440.

298. Singh, H. S.; Mijs, W. J., *Organic Synthesis by Oxidation with Metal Compounds*. Plenum: New York, 1986.

299. Mendel, R. R., *Metallomics and the Cell. Metal Ions in Life Sciences : Metabolism of Molybdenum*. Banci, Lucia ed.; Springer: 2013; Vol. 15.

300. Stiefel, E. I., Transition metal sulfur chemistry and its relevance to molybdenum and tungsten enzymes. In *Pure and Applied Chemistry*, 1998; Vol. 70, p 889.

301. Burke, G. L., *The Corrosion of Metals in Tissues; and An Introduction to Tantalum*. Canadian Medical Association Journal: 1940; Vol. 43.

302. Grzybowski, M.; Skonieczny, K.; Butenschön, H.; Gryko, D. T., *Angew. Chem. Int. Ed.* **2013**, *52*, 9900

303. Sigel, H.; Sigel, A., *Metal Ions in Biological Systems : Vanadium and Its Role in Life*. CRC: 1995; Vol. 31.