

# Structural Study and Solution Integrity of Dioxomolybdenum(VI) Complexes with Tridentate Schiff Base and Azole Ligands

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*Dedicated to Professor Roald Hoffmann with Gratitude and in Recognition to his Seminal Work in Chemistry on the Occasion of his 65<sup>th</sup> Birthday*

**Abstract.** Four new molybdenum complexes [Mo<sup>VI</sup>O<sub>2</sub>(L<sup>1</sup>)(Him)] (**1**), [Mo<sup>VI</sup>O<sub>2</sub>(L<sup>1</sup>)(3-MepzH)] (**2**), [Mo<sup>VI</sup>O<sub>2</sub>(L<sup>2</sup>)(3-MepzH)] (**3**), and [(Mo<sup>VI</sup>O<sub>2</sub>)<sub>2</sub>(μ-L<sup>3</sup>)(MeOH)<sub>2</sub>] (**4**) were synthesized and characterized by IR, NMR, ESI-MS, and single-crystal structure analysis [H<sub>2</sub>L<sup>1</sup> = 2-(salicylideneamino)-2-methyl-1-propanol, H<sub>2</sub>L<sup>2</sup> = 2-(3-methoxysalicylideneamino)-2-methyl-1-propanol, H<sub>4</sub>L<sup>3</sup> = 1,7-bis(salicylidene)dihydrazide malonic acid, Him = imidazole and 3-MepzH = 3-methylpyrazole]. In all four structures the molybdenum atom has a distorted octahedral coordination with the three meridional donor atoms from the Schiff base di- or tetraanion (L<sup>1,2</sup>)<sup>2-</sup>/(L<sup>3</sup>)<sup>4-</sup> and one oxo group occupying the sites of the equatorial plane. The other oxo group and the azole or methanol molecule occupy the apical sites. In **1-3** two centrosymmetrically related

molecules form a hydrogen-bonded pair through the (azole)N-H...O(alkoxo) interaction. Additional crystal packing appears to be controlled mostly by π stacking between the aromatic rings of the salicyl moiety. ESI-MS investigations reveal that the integrity of complexes **1-4** is largely retained in methanol solution. At the same time evidence is provided that di- to tetranuclear oligomers of formula [{Mo<sup>VI</sup>O<sub>2</sub>(L)}<sub>x</sub>] and [{Mo<sup>VI</sup>O<sub>2</sub>(L)}<sub>x</sub>(3-MepzH)] with L = L<sup>1</sup>, L<sup>2</sup>, x = 2, 3, 4 are present simultaneously with **2** and **3** in methanol solution, respectively the tetranuclear species [{(Mo<sup>VI</sup>O<sub>2</sub>)<sub>2</sub>(L<sup>3</sup>)<sub>2</sub>] with **4**.

**Keywords:** Molybdenum; Schiff base; ESI-MS; Hydrogen bonding; π Stacking

## Strukturuntersuchungen und molekulare Assoziation in Lösung von Dioxomolybdän(VI)-Komplexen mit dreizähligen Schiff-Basen und Azol-Liganden

**Inhaltsübersicht.** Vier neue Molybdänkomplexe [Mo<sup>VI</sup>O<sub>2</sub>(L<sup>1</sup>)(Him)] (**1**), [Mo<sup>VI</sup>O<sub>2</sub>(L<sup>1</sup>)(3-MepzH)] (**2**), [Mo<sup>VI</sup>O<sub>2</sub>(L<sup>2</sup>)(3-MepzH)] (**3**) und [(Mo<sup>VI</sup>O<sub>2</sub>)<sub>2</sub>(μ-L<sup>3</sup>)(MeOH)<sub>2</sub>] (**4**) wurden hergestellt und mit IR, NMR, ESI-MS und Einkristall-Röntgenstrukturanalyse charakterisiert [H<sub>2</sub>L<sup>1</sup> = 2-(Salicylideneamino)-2-methyl-1-propanol, H<sub>2</sub>L<sup>2</sup> = 2-(3-Methoxysalicylideneamino)-2-methyl-1-propanol, H<sub>4</sub>L<sup>3</sup> = 1,7-Bis(salicylidene)dihydrazidmalonsäure, Him = Imidazol und 3-MepzH = 3-Methylpyrazol]. In allen vier Strukturen weist das Molybdänatom eine verzerrt-oktaedrische Koordination auf, mit den drei meridionalen Donoratomen des Di- oder Tetraanions (L<sup>1,2</sup>)<sup>2-</sup>/(L<sup>3</sup>)<sup>4-</sup> der Schiff-Base und einer Oxo-Gruppe in der equatorialen Ebene. Die zweite Oxo-Gruppe und das Azol- oder

Methanalmolekül besetzen die apikalen Stellen. In **1-3** sind immer zwei zentrosymmetrisch zueinander in Beziehung stehende Moleküle über (azol)N-H...O(alkoxo) Wasserstoffbrücken paarweise miteinander verknüpft. Die weitere Kristallpackung scheint hauptsächlich durch π-Stapelung zwischen den aromatischen Ringen des Salicylrestes kontrolliert zu werden. ESI-MS Untersuchungen zeigen, dass die Zusammensetzung der Komplexe **1-4** in methanolischer Lösung im wesentlichen beibehalten wird. Gleichzeitig gibt es Hinweise, dass di- bis tetranukleare Oligomere der Formeln [{Mo<sup>VI</sup>O<sub>2</sub>(L)}<sub>x</sub>] und [{Mo<sup>VI</sup>O<sub>2</sub>(L)}<sub>x</sub>(3-MepzH)] mit L = L<sup>1</sup>, L<sup>2</sup>, x = 2, 3, 4 neben **2** und **3** in methanolischer Lösung vorliegen, bzw. die tetranukleare Spezies [{(Mo<sup>VI</sup>O<sub>2</sub>)<sub>2</sub>(L<sup>3</sup>)<sub>2</sub>] von **4**.

### Introduction

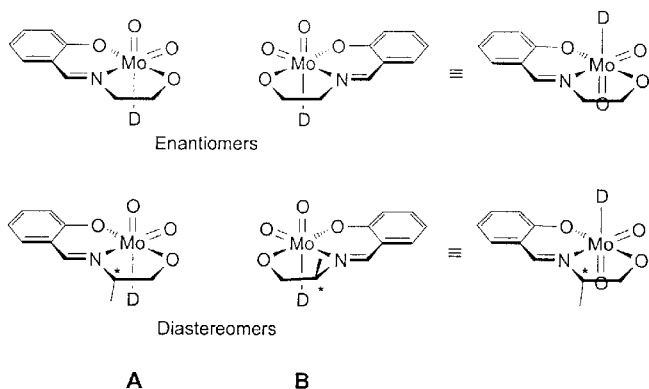
Molybdenum has been found to be a very important element in biological systems. Apart from the nitrogenases in where a molybdenum atom can be a component of the

multinuclear active sites [1], there are a number of mononuclear molybdenum enzymes that are often referred to as oxomolybdenum enzymes [2]. The latter can be divided into two groups: Enzymes from the first group catalyze the oxidative hydroxylation of aldehydes and aromatic heterocycles in reactions that necessarily involve the cleavage of a C-H bond [2,3]. Mononuclear enzymes from the second group catalyze proper oxygen atom transfer reactions to or from an available electron lone pair of substrates [4]. In order to mimic the biological systems, a number of dioxomolybdenum complexes have been synthesized and characterized

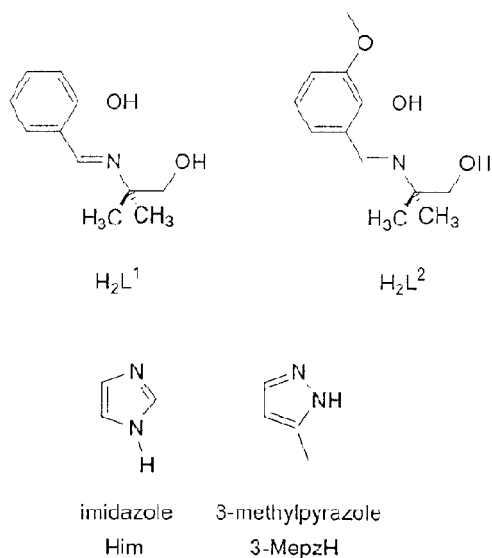
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[5]. The oxygen atom transfer ability of dioxomolybdenum complexes to some substrates is related to the lability of Mo=O bonding.

Recently, Nakajima et al. reported on  $[\text{MoO}_2(\text{L})(\text{D})]$  complexes ( $\text{H}_2\text{L} = (R)\text{-}2\text{-}[(2\text{-hydroxy-}1\text{-naphthyl)methylideneamino]butanol$ , where D is a neutral monodentate ligand such as pyridine or 4,4'-bipyridine or the Mo=O unit from a neighboring molecule [6]. Such dioxomolybdenum complexes with a tridentate Schiff base ligand can have two isomers (A and B) in the solid-state and in solution. The two isomers are enantiomers for an achiral Schiff base or diastereomers in the case of chiral base (enantiomerically pure form). NMR experiments on the diastereomers indicate a rapid isomerization in solution. Isomerization is suggested to proceed via a five coordinate intermediate after dissociation of D so that a partial rotation of the *cis*-MoO<sub>2</sub> moiety becomes possible [6].

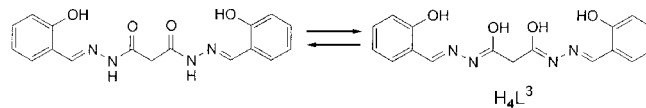


A continuous interest in the chemistry of MoO<sub>2</sub>-complexes [7] and with Schiff base ligands in particular [8] can be noted. We report here the synthesis and characterization of three new dioxomolybdenum(VI) complexes with the Schiff base ligands L<sup>1</sup> and L<sup>2</sup> and a neutral azole ligand.



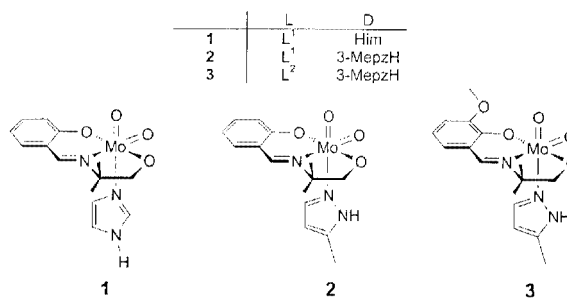
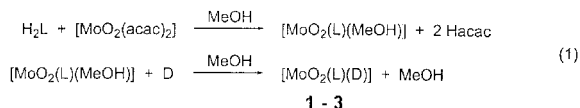
The solution behavior of the complexes was studied by ESI-MS as a means to check their integrity. In addition, a

binuclear dioxomolybdenum(VI) complex with the hexadentate ligand L<sup>3</sup> was synthesized and characterized accordingly.

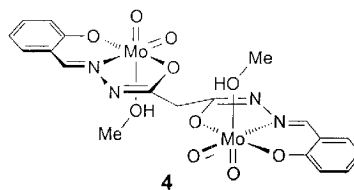
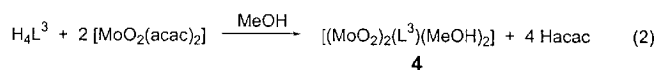


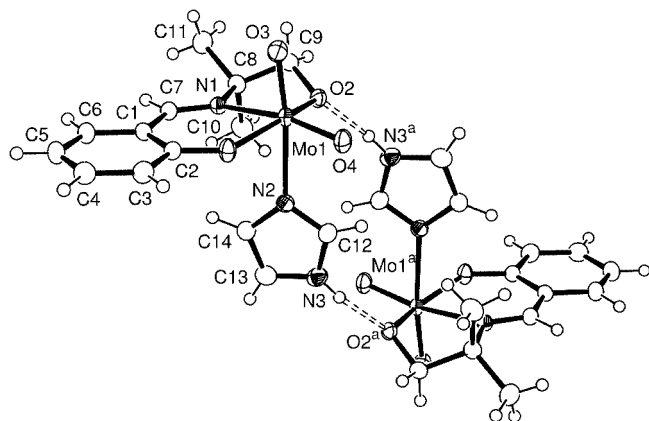
## Results and Discussion

The Schiff-base ligands  $\text{H}_2\text{L}^1$  and  $\text{H}_2\text{L}^2$  were synthesized in-situ from salicylaldehyde and 3-methoxysalicylaldehyde, respectively, with 2-amino-2-methyl-1-propanol and reacted in methanol with bis(acetylacetonato)dioxomolybdenum(VI),  $[\text{MoO}_2(\text{acac})_2]$  to form the intermediate methanol adduct. Upon addition of the azole group the products 1–3 precipitated from the reaction mixture in high yield (eq. (1)). The complexes are yellow solids and could be crystallized from methanol.



The Schiff base malonobis(salicylidenehydrazide) ( $\text{H}_4\text{L}^3$ ) is a hexadentate ligand, which behaves as a dibasic anion in the keto form and as a tetrabasic moiety in the enol form under suitable experimental conditions [9]. The ligand forms binuclear dioxomolybdenum(VI) complexes by utilizing all four hydroxyl groups for the complex formation. The reaction of bis(acetylacetonato)dioxomolybdenum(VI) with  $\text{H}_4\text{L}^3$  in a 2:1 molar ratio in methanol resulted in the formation of a binuclear complex with formula  $[(\text{MoO}_2)_2(\text{L}^3)(\text{MeOH})_2]$  (**4**) and the replacement of all four protons from the ligand (eq. (2)).



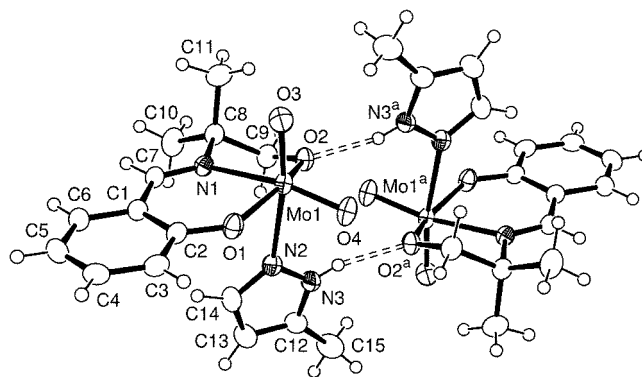


**Fig. 1** Molecular structure of a centrosymmetric hydrogen-bonded pair of complex  $[\text{MoO}_2(\text{L}^1)(\text{Him})]$ , **1**. Symmetry code  $a = -x, 1-y, -z$ .

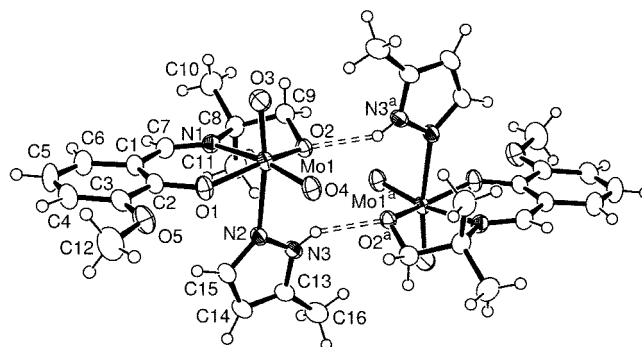
Complex **4** is a yellow solid and soluble in chloroform, DMSO, and a methanol/acetonitrile-mixture. Crystals suitable for X-ray diffraction were obtained from a methanol:acetonitrile (50:50) solution. The crystals contain two molecules of methanol per formula unit as solvent of crystallization.

The molecular structures of **1**, **2**, and **3** are shown in Fig. 1, 2, and 3, respectively. Selected bond distances and angles are listed in Table 1. In all three structures the molybdenum atom has a distorted octahedral coordination with the three donor atoms from the Schiff-base dianion  $(\text{L}^1)^{2-}$  and one oxo group occupying the sites of the equatorial plane. The other oxo group and the imidazole or pyrazole molecule occupy the apical sites. In all three structures two molecules are related by a center of inversion and form a hydrogen-bonded pair through the (azole) $\text{N3-H}\cdots\text{O2(alkoxo)}$  interaction. The two molecules of the pair correspond to the two enantiomeric forms **A** and **B**, shown above. Distances and angles for the hydrogen-bonding interactions are listed in Table 2. Additional crystal packing appears to be controlled mostly by  $\pi$  stacking between the aromatic rings of the salicyl moiety. Parameters for the  $\pi$  stacking and additional  $\text{C-H}\cdots\pi$  interactions are summarized in Table 3. While the molecules in **1** and one of the independent molecules in **2** (see below) show the typical parallel-displaced  $\pi$  interaction, the aromatic rings in **3** exhibit a more seldom close to facial  $\pi$ - $\pi$  alignment, albeit at an increased interplanar separation [10].  $\text{C-H}\cdots\pi$  interactions [11,12] are evident in the structure of **1** and especially of **2** (see below) but not of **3**.

The structure of **2** has two independent molecules in the unit cell. The two molecules have slightly different orientations of the phenyl and the pyrazole ring plane with respect to the  $\text{MoO}_4\text{N}_2$  core. More important, however, the two independent molecules differ in their intermolecular packing arrangement. The molecules of Mo1 feature  $\pi$  stacking interactions as illustrated in Fig. 4 whereas the molecules of Mo2 appear organized by  $\text{C-H}\cdots\pi$  interactions as is evident from Fig. 5. There is no  $\pi$  stacking between the



**Fig. 2** Molecular structure of a centrosymmetric hydrogen-bonded pair of one of the two independent molecules of complex  $[\text{MoO}_2(\text{L}^1)(3\text{-MepzH})]$ , **2**. Symmetry code  $a = 1-x, 1-y, -z$ .



**Fig. 3** Molecular structure of a centrosymmetric hydrogen-bonded pair of complex  $[\text{MoO}_2(\text{L}^2)(3\text{-MepzH})]$ , **3**. Symmetry code  $a = 1-x, -y, -z$ .

molecules of Mo2.  $\text{C-H}\cdots\pi$  interactions control the packing between the molecules of Mo1 and Mo2 (see Table 3).

Compound **3** has a slightly different Schiff base ligand  $(\text{L}^2)$  with a methoxy group at the 3-position of the phenyl ring. Yet, the molecular structure is similar to those of **1** and **2**.

The hexadentate ligand  $\text{L}^3$  forms a binuclear dioxomolybdenum complex whose structure is illustrated in Fig. 6. Selected bond distances and angles for **4** are included in Table 1. The molybdenum atoms have again a distorted octahedral coordination with the donor atoms from the Schiff-base tetraanion  $(\text{L}^3)^{4-}$  and one oxo group occupying the sites of the equatorial planes. The other oxo group occupies the apical sites. Different from **1-3** the remaining apical sites are now occupied by a methanol molecule of solvation. Both molybdenum atoms of the binuclear complex in **4** have the same **A**- or **B**-type configuration. A related structure to **4** of formula  $[(\text{MoO}_2)_2(\text{L}^3)(\text{Me}_2\text{SO})_2]$  is available [13]. No  $\pi$  stacking or relevant  $\text{C-H}\cdots\pi$  interactions are obvious in the crystal structure of **4**.

It is obvious that the Mo-O distances in **1-4** correspond to the different types of oxygen atoms. The  $\text{Mo}=\text{O}_{3,4}$  bond distances lie around  $1.70\pm 0.02$  Å.  $\text{O}=\text{Mo}=\text{O}$  angles are  $106\pm 1^\circ$ . The  $\text{Mo}-\text{O}_2(\text{alkoxo})$  distances are  $1.96\pm 0.01$  Å in **1-3** and  $2.02\pm 0.01$  Å in **4**. They are slightly longer than

**Table 1** Selected bond lengths/Å and angles/° for **1**, **2**, **3**, and **4**<sup>a)</sup>

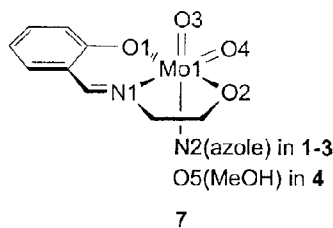
|                | <b>1</b>   | <b>2</b> <sup>b)</sup>                | <b>3</b>   | <b>4</b> <sup>c)</sup>            |
|----------------|------------|---------------------------------------|------------|-----------------------------------|
| Mo=O3          | 1.7123(12) | 1.7067(14) / 1.7022(13) <sup>b)</sup> | 1.7093(14) | 1.691(5) / 1.680(5) <sup>c)</sup> |
| Mo=O4          | 1.7148(12) | 1.7141(13) / 1.7143(13)               | 1.7176(14) | 1.694(5) / 1.694(5)               |
| Mo-O1(phenoxo) | 1.9445(11) | 1.9343(12) / 1.9737(12)               | 1.9468(14) | 1.923(5) / 1.897(4)               |
| Mo-O2(alkoxo)  | 1.9607(11) | 1.9624(12) / 1.9421(12)               | 1.9575(12) | 2.024(5) / 2.014(4)               |
| Mo-N1          | 2.2939(13) | 2.2875(14) / 2.2851(14)               | 2.3039(16) | 2.255(5) / 2.264(5)               |
| Mo-N2(azole)   | 2.3818(14) | 2.4079(16) / 2.3749(15)               | 2.3556(16) | —O5 2.323(5) / O10 2.312(5)       |
| O4-Mo-O3       | 105.90(6)  | 105.21(7) / 105.79(6)                 | 106.13(7)  | 106.8(3) / 105.9(3)               |
| O4-Mo-O1       | 101.91(5)  | 101.85(6) / 99.30(6)                  | 101.88(6)  | 105.1(2) / 105.3(2)               |
| O3-Mo-O1       | 97.93(6)   | 98.81(6) / 96.68(6)                   | 98.64(7)   | 99.6(2) / 99.5(2)                 |
| O4-Mo-O2       | 97.55(5)   | 95.84(6) / 98.04(6)                   | 97.51(6)   | 94.6(2) / 94.4(2)                 |
| O3-Mo-O2       | 95.19(5)   | 99.77(6) / 99.80(6)                   | 97.01(6)   | 97.6(2) / 97.4(2)                 |
| O1-Mo-O2       | 152.49(5)  | 149.91(5) / 151.80(5)                 | 150.52(5)  | 148.6(2) / 149.2(2)               |
| O4-Mo-N1       | 162.98(5)  | 162.18(6) / 161.04(6)                 | 163.76(6)  | 157.5(2) / 158.1(2)               |
| O3-Mo-N1       | 89.85(5)   | 91.40(6) / 92.90(6)                   | 88.98(7)   | 92.9(2) / 93.0(2)                 |
| O1-Mo-N1       | 81.78(5)   | 81.49(5) / 81.33(5)                   | 81.17(5)   | 81.4(2) / 81.7(2)                 |
| O2-Mo-N1       | 74.16(4)   | 74.62(5) / 75.15(5)                   | 74.29(5)   | 71.7(2) / 71.8(2)                 |
| O4-Mo-N2       | 82.41(5)   | 84.77(6) / 83.70(6)                   | 86.77(6)   | —O5 85.4(3) / —O10 86.0(3)        |
| O3-Mo-N2       | 171.69(5)  | 170.01(6) / 170.11(6)                 | 167.05(6)  | —O5 167.5(2) / —O10 167.9(2)      |
| O1-Mo-N2       | 79.96(5)   | 79.01(5) / 78.74(5)                   | 79.35(6)   | —O5 79.0(2) / —O10 78.9(2)        |
| O2-Mo-N2       | 83.58(5)   | 78.59(5) / 81.25(5)                   | 79.82(5)   | —O5 78.6(2) / —O10 79.1(2)        |
| N1-Mo-N2       | 81.91(5)   | 78.65(5) / 77.81(5)                   | 78.07(5)   | —O5 74.6(2) / —O10 74.9(2)        |

<sup>a)</sup> All four complexes have the same atom labelling for the coordination sphere around Mo1, schematically depicted in **7**. O3 is trans to N2(azole) or O5(MeOH) in **4**. O4 is trans to N1. For the labelling of the coordination sphere around Mo2 in **2** and **4** see footnote b and c.

<sup>b)</sup> Two independent molecules (**2**-Mo1 and **2**-Mo2) in the unit cell. The atom numbering in molecule **2**-Mo2 (vs. **2**-Mo1) is O5 (O1), O6 (O2), O7 (O3), O8 (O4), N4 (N1), N2 (N5). The first column gives the distances and angles around Mo1, the second column around Mo2.

<sup>c)</sup> Binuclear complex. The atom number for the donor atoms around Mo2 (vs. Mo1) is O6 (O1), O7 (O2), O8 (O3), O9 (O4), N3 (N1), O10 (O5). The first column gives the distances and angles around Mo1, the second column around Mo2. In **4** there is a methanol molecule in place of the azole ligand. Hence, N2(azole) corresponds to O5 (Mo1) or O10 (Mo2) from CH<sub>3</sub>OH.

Common atom labelling scheme around Mo1:

**Table 2** Hydrogen bonding interactions in **1**, **2**, and **3**

| Compound               | D-H...A    | D-H/Å   | H...A/Å | D...A/Å    | D-H...A/° |
|------------------------|------------|---------|---------|------------|-----------|
| <b>1</b>               | N3-H...O2a | 0.88(3) | 1.88(3) | 2.7580(19) | 172(3)    |
| <b>2</b> <sup>a)</sup> | N3-H...O2a | 0.81(2) | 1.98(2) | 2.764(2)   | 163(2)    |
|                        | N6-H...O6b | 0.77(2) | 2.10(2) | 2.8425(19) | 164(2)    |
| <b>3</b>               | N3-H...O2a | 0.82(2) | 2.10(2) | 2.844(2)   | 150(2)    |

D = Donor, A = acceptor. Symmetry transformations: **1** a = -x, 1-y, -z; **2** a = 1-x, 1-y, -z; **2** b = 2-x, -y, 1-z; **3** a = 1-x, -y, -z;

<sup>a)</sup> Two independent molecules in the unit cell.

the Mo-O1(phenoxo) distances of 1.94±0.01 Å in **1–3** and 1.91±0.02 Å in **4**. The average values are within the range of reported mononuclear tridentate Schiff base MoO<sub>2</sub>-complexes [6,8c,14] and Mo-O distances in general [15]. An exception is one of the two independent molecules in the structure of **2** where the Mo-O2(alkoxo) bond is shorter than the Mo-O1(phenoxo) bond (1.973 vs. 1.942 Å). On the average Mo-O(terminal alkoxo) distances are found to be slightly shorter than Mo-O(aryloxo) distances (1.91±0.05 vs. 1.96±0.08 Å) [15]. Yet, their ranges clearly overlap when

taking into account the standard deviations  $\sigma$  of 0.05 and 0.08 Å, respectively.

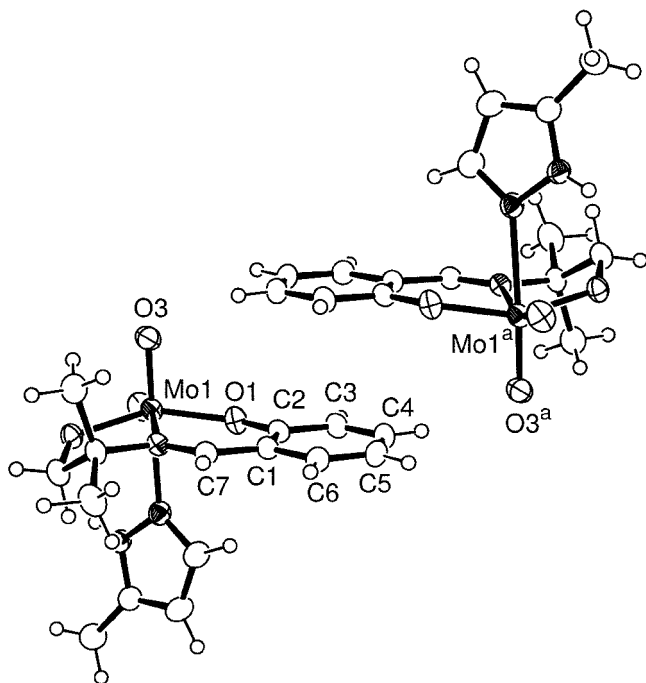
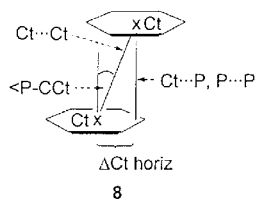
The nitrogen atoms of the Schiff base ligands are *trans* to one of the double bonded oxo groups. The Mo-N(Schiff base) distances are 2.295±0.010 Å for **1–3** and 2.259±0.005 Å for **4**. This is clearly longer than typical Mo<sup>V,VI</sup>-N(Schiff base) distances of 2.124(13) Å [15] but is within the range (2.28–2.50 Å) when nitrogen is *trans* to a double-bonded oxo group. A nitrogen atom of an azole (imidazole or 3-methylpyrazole) molecule occupies an api-

**Table 3**  $\pi$  Stacking and C-H $\cdots\pi$  contacts involving the aromatic salicyl rings in **1–3**<sup>a)</sup>

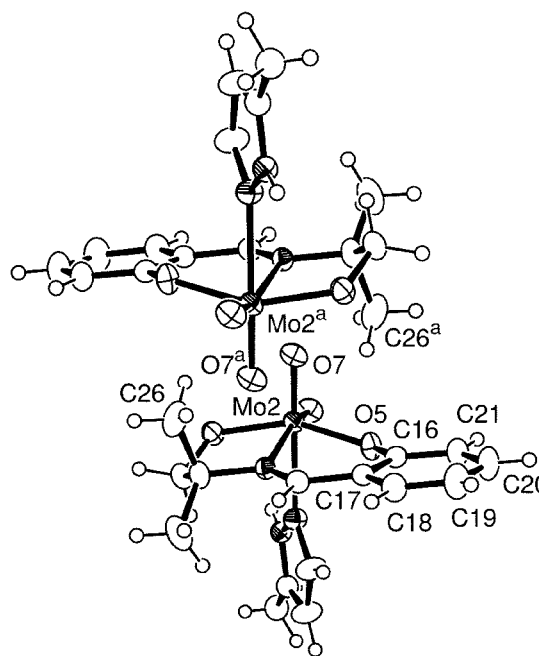
|   | 1                  | 2   | 3  |
|---|--------------------|---|--|
| $\pi$ Stacking <sup>a)</sup>                            |                    | molecule Mo1 only   |  |
| Ct $\cdots$ Ct/ $\text{\AA}$ <sup>b)</sup>              | 3.740              | 3.504   | 3.777  |
| $\langle$ P-P/ $^\circ$ <sup>c)</sup>                   | 0.0                | 0.0   | 0.0  |
| Ct $\cdots$ P, P $\cdots$ P/ $\text{\AA}$ <sup>d)</sup> | 3.580              | 3.284   | 3.759  |
| $\langle$ P-CCt/ $^\circ$ <sup>e)</sup>                 | 16.8               | 20.4  | 5.5  |
| $\Delta$ Ct horiz/ $\text{\AA}$ <sup>f)</sup>           | 1.12               | 1.22  | 0.37   |
| symmetry relation:                                      | $1/2-x, 1/2-y, -z$ | $-x, 1-y, 1-z$  | $2-x, -y, 1-z$   |
| C-H $\cdots\pi$ contacts <sup>a)</sup>                  | C11-H11B           | Mo2 $\cdots$ Mo2 // Mo1 $\cdots$ Mo2<br>C26-H26C // C9-H9B $\cdots$ ring Mo2,<br>C10-H10B $\cdots$ ring Mo2 | no C-H $\cdots\pi$ contacts<br>with C-H $\cdots$ Ct < 3.4 $\text{\AA}$ |
| H $\cdots$ Ct/ $\text{\AA}$ <sup>g)</sup>               | 3.21               | 3.31 // 3.27, 3.11  |  |
| H $\cdots$ P/ $\text{\AA}$ <sup>h)</sup>                | 3.14               | 3.04 // 2.84, 2.95  |  |
| C-H $\cdots$ Ct/ $^\circ$                               | 110.5              | 105.2 // 145.8, 156.8   |  |
| symmetry relation:                                      | $x, -y, 1/2+z$     | $1-x, -y, 1-z$ // $1-x, 1-y, -z$  |  |

<sup>a)</sup> For Ct $\cdots$ Ct <sup>b)</sup> distances < 6.0  $\text{\AA}$ , C-H $\cdots$ Ct distances < 3.4  $\text{\AA}$ . Computations were carried out with PLATON for Windows [30]. No  $\pi$  stacking or relevant C-H $\cdots\pi$  interactions are obvious in the crystal structure of **4**.

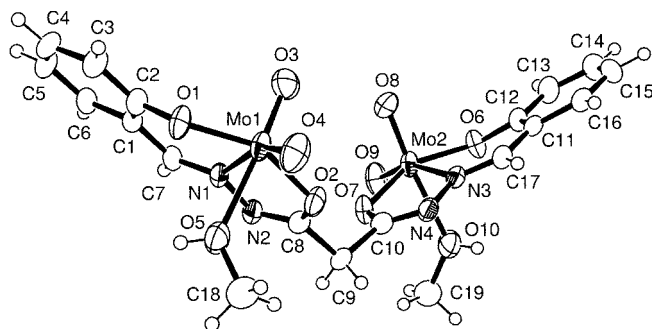
<sup>b)</sup> Ct = ring centroid, Ct $\cdots$ Ct = distance between ring centroids. – <sup>c)</sup>  $\langle$ P-P = dihedral angle between the ring planes. – <sup>d)</sup> Ct $\cdots$ P = perpendicular distance from the centroid onto the other ring plane, the interplanar separation, plane-plane distance P $\cdots$ P. – <sup>e)</sup>  $\langle$ P-CCt = angle between the Ct $\cdots$ Ct vector and the normal to the ring plane. – <sup>f)</sup>  $\Delta$ Ct horiz = horizontal displacement of the ring centroids. Both  $\langle$ P-CCt or  $\Delta$ Ct horiz provide a measure of the ring slippage, i.e. the parallel displacement from a facial alignment. The smaller  $\langle$ P-CCt or  $\Delta$ Ct horiz the better the facial alignment and the smaller the ring slippage. For a graphical depiction of distances and angles in the assessment of  $\pi$  stacking, see **8**. – <sup>g)</sup> H $\cdots$ Ct = distance between hydrogen and ring centroid. – <sup>h)</sup> H $\cdots$ P = perpendicular distance from hydrogen onto the ring plane.



**Fig. 4** The different intermolecular packing among each of the two independent molecules in **2** –  $\pi$  stacking for the molecules of Mo1, for details see Table 3. (C4-)H4 $\cdots$ O3a 2.81  $\text{\AA}$ , 123.4 $^\circ$ . Symmetry code a =  $-x, 1-y, 1-z$ .



**Fig. 5** The different intermolecular packing among each of the two independent molecules in **2**. – C-H $\cdots\pi$  interactions for the molecules of Mo2, for details see Table 3. C-H $\cdots\pi$  interactions between molecules of Mo1 and Mo2 are not shown. (C26-)H26A $\cdots$ O7a 2.81  $\text{\AA}$ , 159.4 $^\circ$ . Symmetry code a =  $1-x, -y, 1-z$



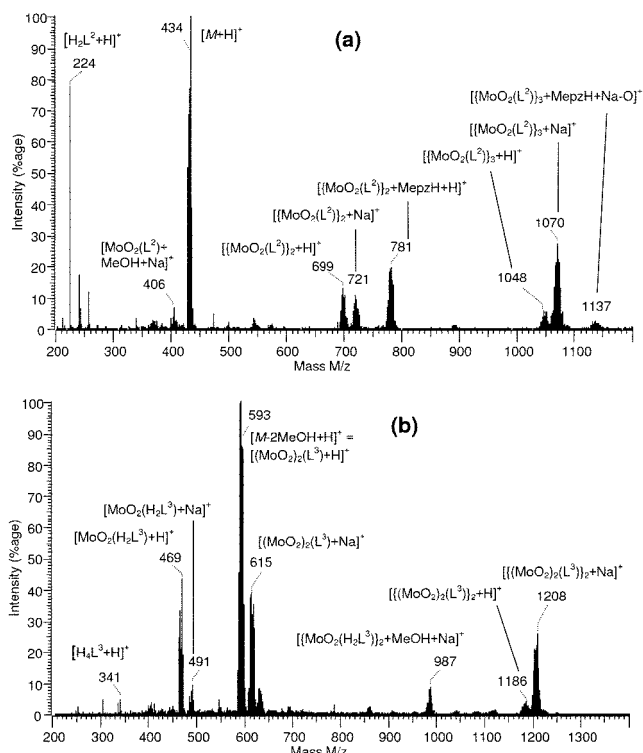
**Fig. 6** Molecular structure of  $[(\text{MoO}_2)_2(\text{L}^3)(\text{MeOH})_2]$ , **4**. The two methanol molecules of crystallization have been omitted.

cal site which is trans to the other double-bonded oxo group in **1–3**. Here, Mo-N(azole) distances range from 2.35 to 2.41 Å. The lengthening with respect to typical Mo-N(imidazole) and Mo-N(pyrazole) distances of  $2.19 \pm 0.06$  Å [15] can again be explained with the position trans to the Mo=O group. The Mo-O(methanol) distances in **4** (2.323(5) and 2.312(5) Å) match the reported average for  $\text{Mo}^{\text{VI}}\text{-O}(\text{alkyl alcohol})$  contacts of  $2.326 \pm 0.035$  Å [15].

Molybdenum(VI) complexes having the formula  $[\text{MoO}_2(\text{L})(\text{D})]$ , where L is a tridentate Schiff base ligand and D is a neutral monodentate ligand, usually display two strong absorption peaks in the IR in the region  $880\text{--}950\text{ cm}^{-1}$  due to the two *cis*- $\text{MoO}_2$  stretches [16]. Two such strong peaks can indeed be assigned in the IR-spectra of **1–4**. A strong peak around  $1630\text{ cm}^{-1}$  is assigned to  $\nu(\text{C}=\text{N})$  and indicates that the N atom coordinates to molybdenum.

X-ray crystallographic characterizations provide valuable structural data on coordination complexes, yet solution studies are also essential. One technique for the characterization of solution species is electrospray ionization mass spectrometry (ESI-MS). The potential of ESI-MS for the characterization of coordination complexes has now been well documented as ESI-MS has been applied to a large range of metal-ligand systems [17]. This very mild technique prevents any fragmentation or artefact formation by reduction or oxidation [18]. Solution ESI-MS spectra can complement the data obtained from solid-state X-ray studies by e.g. by confirming the solution integrity of metal complexes [19]. An advantage of ESI-MS over other MS techniques is the ability to analyze solution species in solvents such as water, methanol and acetonitrile [20].

ESI-MS studies have been carried out on the complexes **1–4** in methanol solution. The original complexes of **1–4** are neutral. However, ion processes in the mass spectrometer allow for the production of  $\text{H}^+$  (from 1% HCOOH or  $\text{CH}_2\text{Cl}_2$ ) that can associate with neutral species. This gives the  $[\text{M}+\text{H}]^+$ -fragment that is detected. The spectrum of **3** is displayed as an example in Fig. 7a. The  $[\text{M}+\text{H}]^+$ -peak is the most intense ion in the spectra. By observation of this molecular ion the solution integrity in methanol of complexes **1–3** was confirmed. Still, the spectra of **2** and **3** show that the pyrazole ligand can be lost and



**Fig. 7** ESI-MS spectrum (positive mode) obtained from  $[\text{MoO}_2(\text{L}^2)(3\text{-MepzH})]$ , **3** in MeOH with 1% HCOOH (a) and from  $[(\text{MoO}_2)_2(\text{L}^3)(\text{MeOH})_2]$ , **4** in MeCN/ $\text{CH}_2\text{Cl}_2$  (b). Note the peaks for multinuclear, oligomeric metal species of the type  $\{[\text{MoO}_2(\text{L}^2)]_x+\text{H}\}^+$  with  $x = 2$  and 3 or with sodium ( $-1/+23$ ) or methylpyrazole ( $+82$ ) for **3** and the tetranuclear species  $\{[(\text{MoO}_2)_2(\text{L}^3)]_2+\text{H}/\text{Na}\}^+$  for **4**.

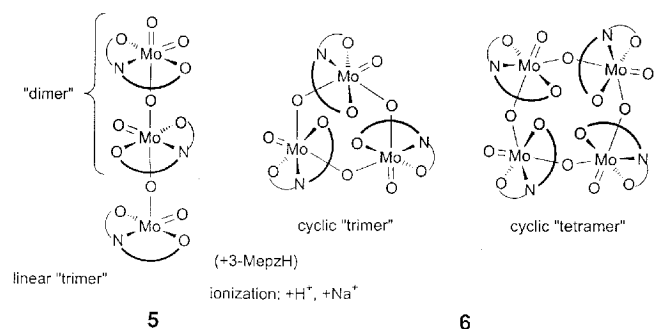
replaced by a methanol ligand, yielding a species  $[\text{MoO}_2(\text{L})+\text{MeOH}+\text{Na}]^+$  albeit with low abundance. Such a species is not seen with **1**. In the spectrum of **4** the base peak is the molecular complex without the two methanol ligands (Fig. 7b). Also visible in the spectrum of **4** is a mononuclear complex  $[\text{MoO}_2(\text{H}_2\text{L}^3)+\text{H}]^+$ , i.e. the ligand  $(\text{H}_2\text{L}^3)^{2-}$  with only one  $\text{MoO}_2^{2+}$  group. Instead of  $\text{H}^+$  association, ionization can also be achieved by addition of ubiquitous  $\text{Na}^+$  to the neutral molecule (see Fig. 7).

The protonated ligand signal  $[\text{H}_2\text{L}+\text{H}]^+$  can also be observed which supposedly arise from some unreacted ligand impurities. The ligand signal may appear high in relative intensity because the production of the  $[\text{M}+\text{H}]^+$ -cation from the neutral parent complex is an inefficient process, whereas protonation of even trace amounts of the free organic Schiff base is very favorable in the gas phase [21].

In the case of molybdenum complexes the isotope distribution from  $^{92}\text{Mo}$  to  $^{100}\text{Mo}$  produces a distinct signature for ion fragments that contain one or more Mo center (see experimental section). Remarkably, in the spectra of **2** and **3** also multinuclear, oligomeric metal species of the type  $\{[\text{MoO}_2(\text{L})]_x+\text{H}\}^+$  are seen with  $x = 2$  and 3. The dinuclear species can in addition contain a methylpyrazole ligand,  $\{[\text{MoO}_2(\text{L})]_2+\text{MepzH}+\text{H}\}^+$ . Ionization by addition of  $\text{Na}^+$  is especially prominent for the oligomeric

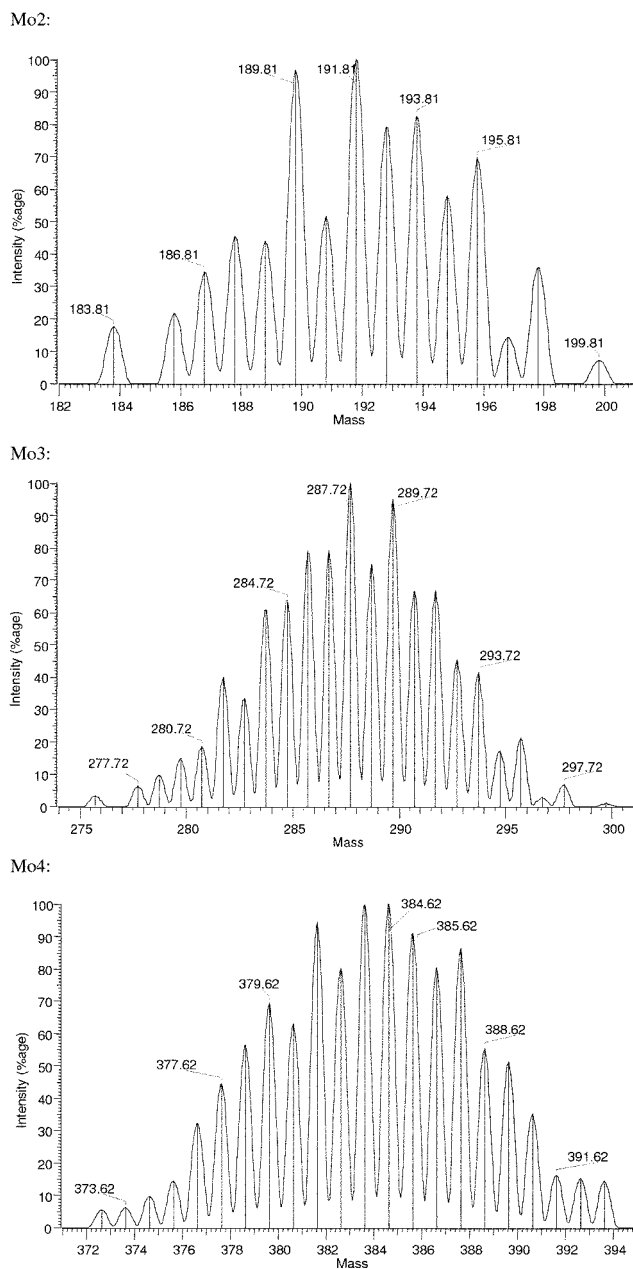
species which may behave as metallacrown ethers. Species such as  $\{[\text{MoO}_2(\text{L})]_x + \text{Na}\}^+$  are seen with  $x = 2$  and 3. The trinuclear oligomer can also contain a methylpyrazole ligand but lacks an oxygen atom to give  $\{[\text{MoO}_2(\text{L})]_3 + \text{MepzH} + \text{Na} - \text{O}\}^+$ . For **2** also a tetranuclear complex of formula  $\{[\text{MoO}_2(\text{L})]_4 + \text{Na}\}^+$  is observed in the mass range up to  $m/z = 1400$ . Analogously for **4** also a tetranuclear species of the type  $\{([\text{MoO}_2]_2(\text{L}^3))_2 + \text{H}/\text{Na}\}^+$  is observed, as well as a dimer for the mononuclear complex of the type  $\{[\text{MoO}_2(\text{H}_2\text{L}^3)]_2 + \text{MeOH} + \text{Na}\}^+$ .

It is suggested that at least part of these multinuclear species are already present in solution and do not form in the ionization chamber of the MS. The multinuclear, "tri- and tetrameric" species may have linear (**5**) or cyclic (**6**) structures. A coordination polymer of a polynuclear dioxomolybdenum(VI) complex with a tridentate Schiff base is known which exhibits a linear  $\text{Mo}=\text{O}\cdots\text{Mo}=\text{O}\cdots$  chain. There, the axial oxo ligand of one molecule coordinates to the sixth site of the molybdenum atom of an adjacent molecule as in **5** [6]. Structures with four  $\text{MoO}_2$  units arranged in an eight membered  $\text{Mo}-\text{O}-\text{Mo}-\text{O}\cdots$  ring [22] or a cluster-type packing [23] are known with nitrogen donor ligands.



## Experimental

NMR spectra were recorded on a Bruker Avance DPX200 or a Varian Unity-300 spectrometer (200.1 or 300.1 MHz, respectively, for  $^1\text{H}$ , 50.3 MHz for  $^{13}\text{C}$ ) with calibration against the solvent signal ( $\text{CD}_3\text{OD}$  3.31 ppm for  $\text{CD}_3$ ,  $d_6$ -DMSO 2.50 ppm for  $^1\text{H}$  and 40.0 ppm for  $^{13}\text{C}$ ). IR spectra were carried out using a Bruker Optic IFS 25 spectrometer as KBr disks. Elemental analysis were done on a VarioEL from Elementaranalysensysteme GmbH. ESI-MS measurements were carried out using a Finnigan MAT TSQ7000 spectrometer with methanol and formic acid (1 %) being the solvent for **1–3** and  $\text{MeCN}/\text{CH}_2\text{Cl}_2$  (10:1) for **4**. Mass spectra were measured in positive mode in the range  $m/z = 200 - 1400$ . Molybdenum containing ions had a clearly visible metal isotope pattern (Fig. 8), arising from the distribution:  $^{92}\text{Mo}$  14.84 %,  $^{94}\text{Mo}$  9.25 %,  $^{95}\text{Mo}$  15.92 %,  $^{96}\text{Mo}$  16.68 %,  $^{97}\text{Mo}$  9.55 %,  $^{98}\text{Mo}$  24.13 %,  $^{100}\text{Mo}$  9.63 % [24]. Peaks were given for the most abundant combinations of the molybdenum isotopes. For  $\text{Mo}_2$ -containing ions the most intense peak stems from  $m/z(\text{Mo}_2) = 191.8$ , with  $m/z(\text{Mo}_2) = 189.8$  of just slightly less intensity. For  $\text{Mo}_3$  the most abundant combinations have  $m/z(\text{Mo}_3) = 287.7$ , followed closely by  $m/z(\text{Mo}_3) = 289.7$ . For  $\text{Mo}_4$   $m/z = 383.6$  and  $384.6$  are essentially of the same intensity, followed closely by  $m/z(\text{Mo}_4) = 381.6$  (see Fig. 8). Because of the overall lower intensities of some of the multinuclear



**Fig. 8** Isotope distribution patterns for  $\text{Mo}_2$ ,  $\text{Mo}_3$  and  $\text{Mo}_4$  species.

species the most abundant combination does not necessarily match with the most intense peak.

**mer-(2-(N-(2-Oxobenzylidene)amino)-2-methyl-1-propanolato-N,O,O')-(imidazole-N)-cis-dioxo-molybdenum(VI),  $[\text{MoO}_2(\text{L}^1)(\text{Him})]$  (**1**).** The complex was prepared in two steps. To a methanolic solution (20 ml) of salicylaldehyde (1.22 g, 0.01 mol) was added 2-amino-2-methyl-1-propanol (0.89 g, 0.01 mol). The resulting yellow solution was stirred at 60 °C for 30 min.  $[\text{MoO}_2(\text{acac})_2]$  (2.94 g, 0.01 mol) was added to this solution with stirring for 1 h. Then, imidazole (1.36 g, 0.02 mol) was added to the solution with stirring. A yellow precipitate occurred and was separated by filtration. Yield 3.48 g (90 % based on Mo). Crystals suitable for X-ray study were obtained by slow evaporation of the solvent from the mother liquor.

Calc. for  $C_{14}H_{17}MoN_3O_4$  (387.25): C 43.42, H 4.42, N 10.85. Found C 43.27, H 4.51, N 10.79 %.

IR (major peaks only): 1628s, 1600s, 1557s, 1396s, 1365s, 1327s, 1069s, 916s ( $\nu_{Mo=O}$ ), 901s ( $\nu_{Mo=O}$ ), 827s, 756s, 737s, 665s, 623s, 542s.

$^1H$  NMR ( $CD_3OD$ ):  $\delta$  1.27 (s, 6H, =N-C(CH<sub>3</sub>)<sub>2</sub>-), 4.26 (s, 2H, -CH<sub>2</sub>-O-), 6.95 (d,  $^3J = 8.0$  Hz, 1H, H3), 7.01 (td,  $^3J = 7.5$  Hz,  $^4J = 1.0$  Hz, 1H, H5), 7.05 (s, 2H, H4,5-imidazole), 7.51 (td,  $^3J = 7.8$  Hz,  $^4J = 1.8$  Hz, 1H, H4), 7.56 (dd,  $^3J = 7.6$  Hz,  $^4J = 1.8$  Hz, 1H, H6), 7.68 (s, 1H, H2-imidazole), 8.54 (s, 1H, -CH=N-); see the numbering schemes below.

ESI-MS: 390  $[M+H]^+$  (100), multinuclear metal containing species could not be clearly seen unlike in the spectra of **2** and **3**.

**mer-(2-(N-(2-Oxobenzylidene)amino)-2-methyl-1-propanolato-N,O,O')-(3-methylpyrazole-N)-cis-dioxo-molybdenum(VI), [MoO<sub>2</sub>(L<sup>1</sup>)(3-MepzH)] (2).** This complex was prepared by a method similar to that used for  $[MoO_2(L^1)(Him)]$  except that 3-methylpyrazole (1.65 g, 0.02 mol) was used instead of imidazole. A yellow solid was obtained by filtration. Yield 3.69 g (92 % based on Mo). Well-shaped crystals suitable for X-ray study were obtained by slow evaporation of the solvent from the mother liquor.

Calc. for  $C_{15}H_{19}MoN_3O_4$  (401.27): C 44.90, H 4.77, N 10.47. Found: C 44.98, H 4.86, N 10.35 %.

IR (major peaks only): 1632s, 1601s, 1572s, 1557s, 1479s, 1446s, 1393s, 1280s, 1113s, 925s ( $\nu_{Mo=O}$ ), 903s ( $\nu_{Mo=O}$ ), 760s, 537s.

$^1H$  NMR ( $CD_3OD$ ):  $\delta$  1.33 (s, 3H, 3-CH<sub>3</sub>-pz), 2.17 (s, 6H, -N-C(CH<sub>3</sub>)<sub>2</sub>-), 4.27 (s, 2H, -CH<sub>2</sub>-O-), 5.95 (s, 1H, H4-pz), 6.95 (d,  $^3J = 8.0$  Hz, 1H, H3), 7.00 (td,  $^3J = 7.5$  Hz,  $^4J = 1.1$  Hz, 1H, H5), 7.4 (s, br, 1H, H5-pz), 7.51 (td,  $^3J = 7.8$  Hz,  $^4J = 1.8$  Hz, 1H, H4), 7.60 (dd,  $^3J = 7.7$  Hz,  $^4J = 1.8$  Hz, 1H, H6), 8.55 (s, 1H, -CH=N-); see the numbering schemes below.

ESI-MS: 376  $[MoO_2(L^1)+MeOH+Na]^+$  (5), 404  $[M+H]^+$  (100), 639  $[MoO_2(L^1)_2+H]^+$  (11), 661  $[MoO_2(L^1)_2+Na]^+$  (7), 721  $[MoO_2(L^1)_2+MepzH+H]^+$  (9), 958  $[MoO_2(L^1)_3+H]^+$  (8), 980  $[MoO_2(L^1)_3+Na]^+$  (4), 1046  $[MoO_2(L^1)_3+MepzH+Na-O]^+$  (2), 1298  $[MoO_2(L^1)_4+Na]^+$  (7).

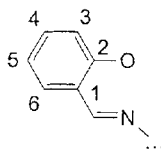
**mer-(2-(N-(2-Oxo-3-methoxybenzylidene)amino)-2-methyl-1-propanolato-N,O,O')-(3-methylpyrazole-N)-cis-dioxo-molybdenum(VI), [MoO<sub>2</sub>(L<sup>2</sup>)(3-MepzH)] (3).** The complex was prepared in two steps. To a methanolic solution (20 ml) of 3-methoxy-salicylaldehyde (1.56 g, 0.01 mol) was added 2-amino-2-methyl-1-propanol (0.89 g, 0.01 mol). The resulting yellow solution was stirred at 60 °C for 30 min.  $[MoO_2(acac)_2]$  (2.94 g, 0.01 mol) was added to this solution with stirring for 1 h. 3-Methyl-pyrazole (1.65 g, 0.02 mol) was then added to the mixture with stirring. A yellow precipitate was observed and separated by filtration. Yield 4.01 g (93 % based on Mo). Crystals suitable for X-ray study were obtained by slow evaporation of the solvent from the mother liquor. Calc. for  $C_{16}H_{21}MoN_3O_5$  (431.30): C 44.56, H 4.91, N 10.47. Found C 44.37, H 5.08, N 10.60 %.

IR (major peaks only): 1639s, 1288s, 1045s, 921s ( $\nu_{Mo=O}$ ), 899s ( $\nu_{Mo=O}$ ), 733s, 532s.

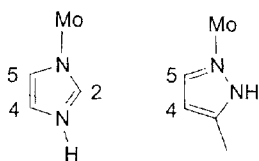
$^1H$  NMR ( $CD_3OD$ ):  $\delta$  1.34 (s, 3H, 3-CH<sub>3</sub>-pz), 2.17 (s, 6H, -N-C(CH<sub>3</sub>)<sub>2</sub>-), 3.77 (s, 3H, CH<sub>3</sub>-O-phenyl), 4.27 (s, 2H, -CH<sub>2</sub>-O-), 5.96 (s, 1H, H4-pz), 7.00 (t,  $^3J = 7.8$  Hz, 1H, H5), 7.51 (td,  $^3J = 7.8$  Hz,  $^4J = 1.8$  Hz, 1H, H4), 7.60 (dd,  $^3J = 7.7$  Hz,  $^4J = 1.8$  Hz, 1H, H6) 7.44 (d, br,  $J = 30.2$  Hz, 1H, H5-pz), 8.53 (s, 1H, -CH=N-); see the numbering schemes below.

ESI-MS: 224  $[H_2L^2+H]^+$  (78 %), 406  $[MoO_2(L^2)+MeOH+Na]^+$  (7), 434  $[M+H]^+$  (100), 699  $[MoO_2(L^2)_2+H]^+$  (13), 721  $[MoO_2(L^2)_2+Na]^+$  (9), 781  $[MoO_2(L^2)_2+MepzH+H]^+$  (19), 1048  $[MoO_2(L^2)_3+H]^+$  (5), 1070  $[MoO_2(L^2)_3+Na]^+$  (27), 1137  $[MoO_2(L^2)_3+MepzH+Na-O]^+$  (2); the spectrum is shown in Fig. 7a.

numbering scheme for the aromatic ring of the salicylidene moiety:



numbering schemes for imidazole and pyrazole:



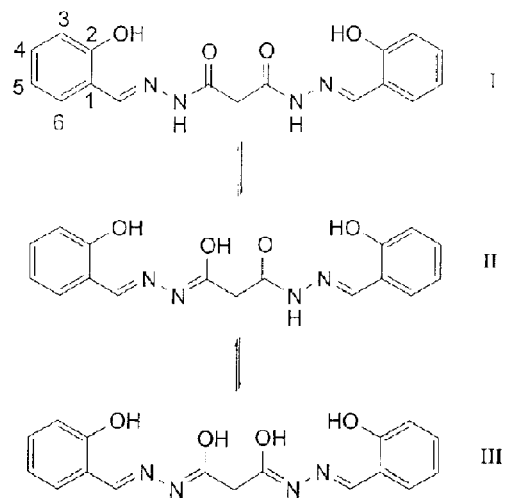
1,7-Bis(salicylidene)dihydrazide malonic acid ( $H_4L^3$ ). The dihydrazide of malonic acid was obtained by the general procedure of condensation of the diethyl ester of malonic acid with hydrazine hydrate [25]. This dihydrazide of malonic acid (1.32 g, 0.01 mol) was dissolved in 100 ml of methanol. Salicylaldehyde (2.44 g, 0.02 mol) was added to the solution and the resulting reaction mixture was refluxed for 2 h. The white solid, which formed on cooling, was separated by filtration, washed with cold methanol and dried in vacuo. Yield 3.23 g (95 %).

Calc. for  $C_{17}H_{16}N_4O_4$  (340.34): C 60.00, H 4.74, N 16.46. Found C 59.48, H 4.78, N 16.56 %.

$^1H$  NMR ( $d_6$ -DMSO):  $\delta$  3.33 (s, I), 3.62 (s, II), 3.91 (s, III) (ratio 1:2:1, 2H, -CH<sub>2</sub>-), 6.67-6.76, 6.83-6.93, 7.14-7.32, 7.52-7.66 (4 sets of multiplets, 8H, aromatic protons), 8.28 (s, I and II, -CH=N-NH-), 8.42 (s, II and III, -CH=N-N=) (ratio 1:1, 2H), 9.99, 10.00 (2H), 11.07, 11.10 (2H), 11.41, 11.49 (2H) (the two signals in each of the aforementioned three groups are of almost equal height giving an appearance of doublets), 11.86 (s, 2H) (Ar-OH, -C-OH, =N-NH-C). The seven signals from 9.99 to 11.86 and also the three signals from 3.33 to 3.91 ppm disappear upon addition of  $CD_3OD$  due to H/D exchange.

$^{13}C$  NMR ( $d_6$ -DMSO):  $\delta$  40.2 (-CH<sub>2</sub>-, III), 41.3 (-CH<sub>2</sub>-, II) (overlapping with the DMSO septet), 42.0 (-CH<sub>2</sub>-, I), 116.42, 116.46, 116.70, 116.72 (C3), 118.96, 119.01, 119.58, 119.62, 119.70 (C1), 120.56, 120.61 (C5), 126.71, 126.81, 129.67, 129.71 (C6), 131.26, 131.40, 131.66, 131.81 (C4), 140.79, 140.96, 147.04, 147.66, 156.63, 156.67, 156.65, 157.71, 162.78, 163.29 (C2, -C=N-NH-, -C=N-N= and -NH-C(OH)-), 168.67, 169.18 (-N=C(O)-, I and II); see the numbering schemes below.

The number of NMR signals for  $H_4L^3$  can only be explained by assuming at least three different tautomeric isomers I-III.



The  $^1H$  NMR spectral features, e.g. three signals for the -CH<sub>2</sub>- groups and two signals for the -CH=N-groups could be reproduced in the calculated spectra for I-III with the ACD/HNMR spectrum generator [26]. The calculated signals for -CH<sub>2</sub>- were 3.07 (I), 3.80 (II), and 3.93 (III). The -CH=N-signals were calculated at 8.08 for -CH=N-NH- in I and II and at 8.67 for -CH=N-N= in II and III. The assignment in the experimental spectra was based on the theoretical calculations.

**[ $\mu$ -mer-2,2'-(4,6-Dihydroxy-2,3,7,8-tetraaza-1,3,6,8-nonatetraene-1,9-diyl)diphenolato-N<sup>2</sup>,O,O',N<sup>8</sup>,O',O<sup>6</sup>]-bis(methanol)-cis-dioxo-molybdenum(VI),  $[MoO_2]_2(\mu-L^3)(CH_3OH)_2 \cdot 2CH_3OH$  (**4** · 2CH<sub>3</sub>OH).** The ligand  $H_4L^3$  (0.34 g, 1.0 mmol) was dissolved in methanol and treated with 0.65 g (2.0 mmol) of  $[MoO_2(acac)_2]$ . The resulting yellow slurry was heated to reflux and stirred for 30 min. Filtration afforded the yellow solid, which was washed with cold methanol and diethyl ether. The crystalline complex was prepared by recrystallization from a methanol-acetonitrile mixture (50:50).



**Table 4** Crystal data for complex **1**, **2**, **3**, and **4**

| Compound  | <b>1</b>  | <b>2</b>  | <b>3</b>  | <b>4</b> · 2CH <sub>3</sub> OH   |
|---|---|---|---|--|
| Empirical formula   | C <sub>14</sub> H <sub>17</sub> MoN <sub>3</sub> O <sub>4</sub> | C <sub>15</sub> H <sub>19</sub> MoN <sub>3</sub> O <sub>4</sub> <sup>a)</sup> | C <sub>16</sub> H <sub>21</sub> MoN <sub>3</sub> O <sub>5</sub> | C <sub>21</sub> H <sub>28</sub> Mo <sub>2</sub> N <sub>4</sub> O <sub>12</sub> |
| Formula weight  | 387.25  | 401.27  | 431.30  | 720.35   |
| Crystal colour  | yellow  | yellow  | yellow  | yellow   |
| Crystal size/mm <sup>3</sup>  | 0.56×0.28×0.20  | 0.55×0.40×0.30  | 0.35×0.30×0.12  | 0.42×0.33×0.20   |
| Temperature/K   | 173(2)  | 173(2)  | 173(2)  | 233(2)   |
| Crystal system  | Monoclinic  | Triclinic   | Monoclinic  | Triclinic  |
| Space group   | C2/c  | P-1   | P <sub>2</sub> /n   | P-1  |
| Unit cell dimensions  |   |   |   |  |
| <i>a</i> /Å   | 31.249(4)   | 11.918(2)   | 8.7235(13)  | 7.7717(10)   |
| <i>b</i> /Å   | 6.7800(8)   | 12.120(2)   | 14.562(2)   | 12.635(3)  |
| <i>c</i> /Å   | 14.2757(17)   | 12.937(2)   | 14.770(3)   | 15.687(2)  |
| $\alpha$ /°   | 90  | 76.670(3)   | 90  | 74.26(1)   |
| $\beta$ /°  | 92.406(2)   | 72.172(3)   | 104.341(13)   | 75.69(1)   |
| $\gamma$ /°   | 90  | 69.681(3)   | 90  | 72.18(2)   |
| <i>V</i> /Å <sup>3</sup>  | 3021.9(6)   | 1651.9(5)   | 1817.9(6)   | 1388.7(4)  |
| <i>Z</i>  | 8   | 4   | 4   | 2  |
| <i>D</i> <sub>calc</sub> /g cm <sup>-3</sup>  | 1.702   | 1.613   | 1.576   | 1.723  |
| $\mu$ /mm <sup>-1</sup>   | 0.890   | 0.817   | 0.752   | 0.969  |
| Reflections (total)   | 12037   | 19302   | 14794   | 12377  |
| Reflections indpt / <i>R</i> <sub>int</sub>   | 4349/0.0247   | 9291/0.0205   | 5245/0.0307   | 6378/0.114   |
| Reflections obs. [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]   | 3812  | 7923  | 4177  | 4266   |
| $\theta$ Range/°  | 2.61-31.01  | 1.67-30.87  | 2.00-30.92  | 1.37-28.23   |
| Data/restraints/parameters  | 4349/0/267  | 9291/0/567  | 5245/0/310  | 6378/0/358   |
| <i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> [ <i>I</i> >2 $\sigma$ ( <i>I</i> )] <sup>b)</sup> | 0.0245/0.0637   | 0.0262/0.0711   | 0.0286/0.0684   | 0.0769/0.1924  |
| <i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all data) <sup>c)</sup>                           | 0.0296/0.0659   | 0.0324/0.0734   | 0.0436/0.0734   | 0.0999/0.2149  |
| Goodness-of-fit on <i>F</i> <sup>2</sup> <sup>d)</sup>  | 1.068   | 1.078   | 1.061   | 1.000  |
| Largest diff. Peak/e Å <sup>-3</sup>  | 0.910   | 0.671   | 0.640   | 0.855  |

<sup>a)</sup> two independent molecules in the unit cell – <sup>b)</sup>  $R_1 = [\sum(|F_o| - |F_c|)] / \sum|F_o|$  – <sup>c)</sup>  $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$  – <sup>d)</sup> Goodness-of-fit =  $[\sum[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$

The resulting crystals were suitable for X-ray analysis. Yield 0.65 g (90 %).

Calc. for C<sub>21</sub>H<sub>28</sub>Mo<sub>2</sub>N<sub>4</sub>O<sub>12</sub> (720.35) C 35.02, H 3.92, N 7.78 Found C 34.91, H 4.08, N 7.86 %.

<sup>1</sup>H NMR (d<sub>6</sub>-DMSO):  $\delta$  3.16 (d, <sup>3</sup>J = 4.5 Hz, 6 H, CH<sub>3</sub>OH), 3.55 (s, 2H, -C(O)-CH<sub>2</sub>-C(O)-), 4.05 (d, <sup>3</sup>J = 4.8 Hz, 2H, CH<sub>3</sub>OH), 6.92 (d, <sup>3</sup>J = 8.2 Hz, 2H, H3), 7.06 (td, <sup>3</sup>J = 7.4 Hz, <sup>4</sup>J = 0.7 Hz, 2H, H5), 7.51 (td, <sup>3</sup>J = 7.8 Hz, <sup>4</sup>J = 1.7 Hz, 2H, H4), 7.56 (dd, <sup>3</sup>J = 7.8 Hz, <sup>4</sup>J = 1.5 Hz, 2H, H6), 8.78 (s, 2H, -CH=N-). <sup>13</sup>C NMR (d<sub>6</sub>-DMSO):  $\delta$  35.1 (-CH<sub>2</sub>-), 49.0 (CH<sub>3</sub>OH), 118.9 (C3), 120.4 (C1), 121.9 (C5), 134.7 (C6), 135.3 (C4), 156.3 (C2), 159.8 (-C=N-N=), 170.3 (-N=C(O)-); see the numbering scheme above.

ESI-MS: 341 [H<sub>4</sub>L<sup>3</sup>+H]<sup>+</sup> (5 %), 469 [MoO<sub>2</sub>(H<sub>2</sub>L<sup>3</sup>+H)]<sup>+</sup> (43), 491 [MoO<sub>2</sub>(H<sub>2</sub>L<sup>3</sup>+Na)]<sup>+</sup>, 593 [M-2MeOH+H]<sup>+</sup> = [(MoO<sub>2</sub>)<sub>2</sub>(L<sup>3</sup>+H)]<sup>+</sup> (100), 615 [(MoO<sub>2</sub>)<sub>2</sub>(L<sup>3</sup>+Na)]<sup>+</sup> (39), 987 [(MoO<sub>2</sub>(H<sub>2</sub>L<sup>3</sup>))<sub>2</sub>+MeOH+Na]<sup>+</sup> (9), 1186 [(MoO<sub>2</sub>)<sub>2</sub>(L<sup>3</sup>)<sub>2</sub>+H]<sup>+</sup> (4), 1208 [(MoO<sub>2</sub>)<sub>2</sub>(L<sup>3</sup>)<sub>2</sub>+Na]<sup>+</sup> (25); the spectrum is displayed in Fig. 7b.

### Structure determination

Diffraction data were collected by the  $\omega$ -scan method with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and the use of a graphite monochromator on a Siemens Bruker Smart CCD for all four complexes. The structures were solved by direct methods (SIR97 for **1–3** and SHELXS-97 for **4**) [27,28]; refinement was done by full-matrix least squares on *F*<sup>2</sup> using the SHELXL-97 program suite [28]. All non-hydrogen positions were found and refined with anisotropic temperature factors. The hydrogen atoms were found from the difference Fourier synthesis and refined isotropically with free temperature factors for **1–3**. Hydrogen atoms for **4** were calculated using appropriate riding models and isotropic temperature factors of U(H) = 1.2 U<sub>eq</sub>(C). Crystal data are listed in Table 4. Graphics were obtained with ORTEP 3 for Windows [29]. Displacement ellipsoids are drawn at the 50 % probability level and H atoms are

shown as spheres of arbitrary radii. Special computations for the crystal structure discussions were carried out with PLATON for Windows [30]. The structural data has been deposited with the Cambridge Crystallographic Data Center (No. CCDC-176926 for **1**, CCDC-176927 for **2**, CCDC-176928 for **3**, and CCDC-176929 for **4**).

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