

Scientific paper

Synthesis and Crystal Structures of Two Novel Molybdenum(V) Complexes with Glycine and D,L-Valine

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Dedicated to the memory of Professor Ljubo Golič

Abstract

Two novel molybdenum(V) complexes, $[\text{Mo}_2\text{O}_4(\text{acac})_2(\text{gly})](\text{EtOH})(\text{H}_2\text{O})$, **1**, and $[\text{Mo}_2\text{O}_4(\text{acac})_2(\text{D,L-val})]$, **2**, (acac = acetylacetonato, EtOH = ethanol), were synthesized by the reaction of $[\text{Mo}_2\text{O}_3(\text{acac})_4]$ and amino acids glycine and D,L-valine, respectively. The complexes were characterized by elemental and IR spectral analysis. Their structures were determined by the single crystal X-ray diffraction method. Both complexes are dinuclear, with singly bonded Mo—Mo in the $\{\text{Mo}_2\text{O}_4\}^{2+}$ core, a carboxylato bridging amino acid, and with each Mo atom additionally coordinated by a bidentate acetylacetonato ligand. Crystal data: $\text{C}_{14}\text{H}_{27}\text{Mo}_2\text{NO}_{12}$ (**1**) crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 8.439(2)$, $b = 20.613(4)$, $c = 12.639(3)$ Å, $\beta = 98.410(10)^\circ$, $Z = 4$; $\text{C}_{15}\text{H}_{25}\text{Mo}_2\text{NO}_{10}$ (**2**) crystallizes in the orthorhombic system, space group $Pbca$ with $a = 13.596(1)$, $b = 19.346(1)$, $c = 15.080(1)$ Å, $Z = 8$.

Keywords: Molybdenum(V) complexes; crystal structure; amino acid complexes

1. Introduction

Molybdenum is an essential metal in almost all organisms and occurs in many enzymes.¹ The importance of investigating molybdenum complexes with amino acids as possible molybdoenzyme model compounds was recognized as long as 40 years ago.^{2,3} The dinuclear fragment $\{\text{Mo}_2\text{O}_4\}^{2+}$, which is also present in the two structures described here, can often be found as the building unit in the chemistry of molybdenum(V). In this fragment each molybdenum atom is bound to two bridging oxygen atoms and one terminal oxygen atom. There can also be an additional ligand such as the carboxylato group acting as a bridging $\mu_2, \eta^1 : \eta^1$ (O,O') ligand.^{4,5} Structures of many acetato complexes of molybdenum(V) with the $\{\text{Mo}_2\text{O}_4\}^{2+}$ units as building block are known. They can be dinuclear⁶ or can assemble into oligonuclear species.^{6,7} Molybdenum atoms in the dinuclear complexes can also

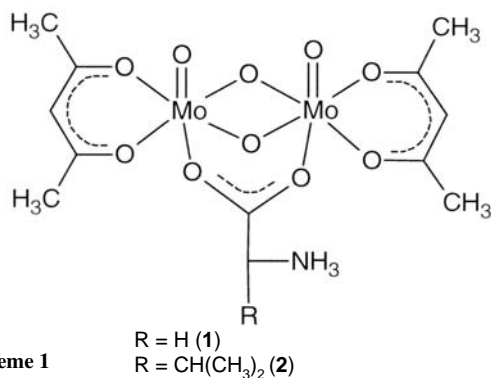
be doubly bridged by sulphur atoms as in $[\text{Mo}_2\text{O}_2\text{S}_2(\text{histidine})_2]$ ⁸ or $[\text{Mo}_2\text{O}_2\text{S}_2(\text{L-cysteine})_2]$.⁹

The first crystal structures of dinuclear molybdenum(V) complexes with the $\{\text{Mo}_2\text{O}_4\}^{2+}$ core and with amino acids as ligands were those of $[\text{Mo}_2\text{O}_4(\text{L-his})_2] \cdot 3\text{H}_2\text{O}$ ¹⁰ and $\text{Na}_2[\text{Mo}_2\text{O}_4(\text{L-cys})_2] \cdot 5\text{H}_2\text{O}$.¹¹ However in these two structures the amino acid is not bridging, the L-histidinato ligand is tridentately *N,N,O*-bound to each Mo, while the L-cysteinato ligand is *S,N,O*-bound to each molybdenum atom. The structure of $\text{Na}_2[\text{Mo}_2\text{O}_4(\text{L-cys})_2] \cdot 5\text{H}_2\text{O}$ was later redetermined by neutron diffraction.¹² The crystal structure of another polymorph of $[\text{Mo}_2\text{O}_4(\text{L-his})_2] \cdot 3\text{H}_2\text{O}$ was recently determined and a similar molecular structure as that of Knox and Prout was found.¹³

Two structures of binuclear complexes with the $\{\text{Mo}_2\text{O}_4\}^{2+}$ core and with molybdenum atoms bridged through the carboxylic atoms of the corresponding amino

acid are known. One is the structure of μ -glycine-*O*:*O'*- μ -oxo-bis[(glycinato-*N,O*)oxomolybdenum(V)]¹⁴ where one glycine is μ_2 -bridging and the other is a glycinato ligand that is *N,O*-bound to each molybdenum. The other is that of $[\text{Mo}_2\text{O}_4(\text{acac})_2\text{thala}] \cdot 3\text{EtOH}$ (acac = acetylacetonato; thala = 3-(2-thienyl)-D,L-alanine).¹⁵ Several structures that have $\{\text{Mo}_2\text{O}_4\}^{2+}$ fragments linked into polynuclear complexes with bridging amino acids, mostly glycine or alanine, have been reported.^{16–21}

In this paper, we report the synthesis and crystal structures of two new dinuclear complexes of molybdenum with amino acids: di- μ -oxo- μ -[glycine-*O*:*O'*]-bis[oxo(2,4-pentanedionato)molybdate(V)] solvated with ethanol and water, $[\text{Mo}_2\text{O}_4(\text{acac})_2(\text{gly})] \cdot (\text{EtOH})(\text{H}_2\text{O})$, **1**, and di- μ -oxo- μ -[D,L-valine-*O*:*O'*]-bis[oxo(2,4-pentanedionato)molybdate(V)], $[\text{Mo}_2\text{O}_4(\text{acac})_2(\text{D,L-val})]$, **2**, (Scheme 1). Both complexes were characterized by chemical analysis and IR spectroscopy, and their crystal structures were determined by single crystal X-ray diffraction.



Scheme 1

2. Experimental

2.1. Materials and Methods

All solvents and chemicals were of commercial reagent grade; all reactions were carried out under an atmosphere of purified nitrogen. Complex $[\text{Mo}_2\text{O}_3(\text{acac})_4]$ was prepared as described in literature.^{22,23} The IR spectra were recorded on a FTIR 1600 Fourier-transform spectrophotometer, using the KBr pellet technique, in the 4500–450 cm^{-1} region. Molybdenum was analytically determined according to the procedure given in the literature.²⁴

2.2. Synthesis and Characterization

Di- μ -oxo- μ -[glycine-*O*:*O'*]-bis-[oxo(2,4-pentanedionato)molybdate(V)]-ethanol(1/1)-water(1/1), $[\text{Mo}_2\text{O}_4(\text{acac})_2(\text{gly})](\text{EtOH})(\text{H}_2\text{O})$, **1**

$\text{Mo}_2\text{O}_3(\text{acac})_4$ (0.635 g, 1 mmol) was dissolved in 20 ml of boiling ethanol in a nitrogen atmosphere. The dark red mixture was hot filtered, heated again till boiling, an aqueous solution of glycine (0.075 g of glycine in 1.5 ml

of boiled water) was then added and heated in nitrogen stream for several hours. After several days at room temperature red-brown crystalline product was obtained. Anal. Calc. For $\text{Mo}_2\text{O}_{12}\text{C}_{14}\text{H}_{27}\text{N}$: C, 28.33, H, 4.55, N, 2.36%. found: C, 23.26, H, 3.31, N, 2.76%. IR(KBr), (cm^{-1}): 1556(s); 1421(m); 964(s); 741(m).

Di- μ -oxo- μ -[D,L-valine-*O*:*O'*]-bis[oxo(2,4-pentanedionato)molybdate(V)], $[\text{Mo}_2\text{O}_4(\text{acac})_2(\text{D,L-val})]$, **2**

0.635 g of $\text{Mo}_2\text{O}_3(\text{acac})_4$ (1 mmol) was dissolved in 35 ml ethanol, boiled under nitrogen atmosphere and then hot filtered. A solution of D,L-valine (0.117 g, 1 mmol) was added to the filtrate and heated for several hours. On the next day, light-red crystals of **2** were obtained. Anal. Calc. for $\text{Mo}_2\text{O}_{10}\text{C}_{15}\text{H}_{25}\text{N}$: C, 31.53, H, 4.37, N, 2.45%. found: C, 31.63, H, 4.28, N, 2.37%. IR(KBr), (cm^{-1}): 1612(s); 1431(m); 961(s); 743(m).

2.3. X-ray Structure Analysis

Single, red colored, crystals of **1** and **2** were grown by slow evaporation of the corresponding solutions obtained from the above described preparations. The X-ray diffraction intensities for compound **1** were collected at room temperature on a Philips PW1100 diffractometer updated by Stoe and Cie²⁵ using Mo- K_α radiation ($\lambda = 0.7107 \text{ \AA}$) with the scan mode. Data were reduced using X-RED.²⁶ Intensity data for compound **2** were collected at 200 K on a Nonius KappaCCD diffractometer with graphite-monochromated Mo- K_α radiation and the data were reduced using the DENZO²⁷ program. The crystal structures were solved by direct methods using the SHELXS97²⁸ program. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations based on F^2 with the SHELXL97²⁹ program. Hydrogen atoms in **1** could be found in the difference Fourier map, however, since the geometry was poor they were placed at ideal calculated positions (aromatic, secondary), or using the rotating group refinement (methyl, amino, hydroxyl groups) with atoms placed at density maxima. The displacement parameters were taken as 1.2 times (aromatic, secondary), and 1.5 times of their parent atoms (methyl, amino and hydroxyl groups, H₂O molecule). For the H₂O molecule one hydrogen atom was found in the difference Fourier map while the other was calculated using CALC-OH³⁰ and was included in the refinement with restrained geometry. In **2** all hydrogen atoms were located in the difference Fourier maps and refined isotropically. Geometry calculations were done using PLATON³¹ and PARST^{32,33} and the structure drawings were prepared using PLATON and PLUTON programs. Crystal data and refinement details are listed in Table 1.

Compound **2** is a racemic compound. Although a mechanical mixture of two enantiomers is sometimes possible (racemic conglomerate), this was not observed in our case.

Table 1. Crystal data, data collection and structure refinement for compounds **1** and **2**.

Compound	1	2
Empirical formula	C ₁₄ H ₂₇ Mo ₂ NO ₁₂	C ₁₅ H ₂₅ Mo ₂ NO ₁₀
Formula weight	593.25	571.24
Crystal system	monoclinic	orthorhombic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>
Unit cell dimensions (Å, °)		
<i>a</i> (Å)	8.439(2)	13.596(1)
<i>b</i> (Å)	20.613(4)	19.346(1)
<i>c</i> (Å)	12.639(3)	15.080(1)
α (°)	90	90
β (°)	98.410(10)	90
γ (°)	90	90
<i>V</i> (Å ³)	2175.0(8)	3966.5(4)
<i>Z</i>	4	8
<i>T</i> (K)	293(2)	200(2)
<i>D</i> _{calc} (g cm ⁻³)	1.812	1.913
μ (MoK _α) (mm ⁻¹)	1.212	1.318
<i>F</i> (000)	1192	2288
Ranges of <i>h, k, l</i>	-11 to 11, 0 to 29, 0 to 17	-19 to 19, -27 to 27, -21 to 21
Reflections collected ^a / unique / observed	6561/6310/2527	11490/6045/5488
Data/restraints/parameters	6310/0/271	6045/0/353
Goodness of fit on <i>F</i> ²	0.961	1.068
<i>R</i> ^b & <i>wR</i> ^c	0.066, 0.102	0.022, 0.054
Largest diff. peak & hole/(e Å ⁻³)	0.610, -0.747	0.442, -0.701

^avalue for **2** refers to unique data but with unmerged Friedel pairs ^b*R* = Σ||*F*_o| - *F*_c|| / Σ|*F*_o| ^c*wR* = [Σ*w*(*F*_o² - *F*_c²)/Σ*w*(*F*_o²)]^{1/2}

The crystallographic data for compounds **1** and **2** have been deposited with the Cambridge Crystallographic Data Center as supplementary material with the deposition numbers: CCDC 682621 for **1** and 682622 for **2**. Copies of the data can be obtained, free of charge via <http://www.ccdc.cam.ac.uk/const/retrieving.html>.

3. Results and Discussion

By direct reaction of [Mo₂O₃(acac)₄] with the amino acids glycine and valine, dinuclear molybdenum complexes **1** and **2** with triply bridged molybdenum atoms were prepared. The diamagnetism of both complexes together with the short Mo–Mo bond indicate presence of a metal-metal bond. IR data indicate presence of the {Mo₂O₄}²⁺ moiety. Absorption maxima that were found in the 1000–900 cm⁻¹ and 750–700 cm⁻¹ region are characteristic of the stretching of isolated Mo=O and the bridging Mo–O–Mo, respectively. Maxima typical for the acetylacetonate ligand and the amino acids were also found (Table 2).

3. 1. Molecular Structures of 1 and 2

Both complexes are dinuclear, with a {Mo₂O₄}²⁺ core. The Mo(μ₂-O)₂Mo moiety is not planar. The fold angle is 165.81(16)° and 163.96(5)°, in **1** and **2**, respectively. The two molybdenum atoms are bridged by the carboxylato group from the amino acid (glycine in **1**, Fig. 1, and valine in **2**, Fig. 2), and with each Mo atom additionally coordinated by a bidentate acetylacetonato ligand. Selected bond distances and angles are given in Table 3. The Cambridge Structural Database³⁴ was searched for structures containing the {Mo₂O₄}²⁺ core, with a bridging carboxylato group, and with two additional oxygen atoms coordinated to each molybdenum atom. The search gave 26 hits. After suppressing outliers from polynuclear structures, the following ranges and mean values were found for 28 such structural fragments: Mo–Mo distances from 2.549 to 2.602 Å, mean value 2.57 Å; Mo=O 1.653 – 1.699 Å, mean 1.68 Å, Mo–O_b 1.916–1.962 Å, mean 1.94 Å; Mo–O_{carboxyl} 2.221 – 2.419 Å, mean 2.34 Å; angle Mo–O_b–Mo 81.94 – 84.77°, mean 83°. Oxygen atoms

Table 2. Characteristic IR absorption maxima (cm⁻¹) in **1** and **2**

	Characteristic IR absorption maxima (cm ⁻¹)					
	ν(O–H)	ν(N–H)	ν _{as} (C=O)	ν _s (C=O)	ν(Mo=O)	ν(Mo–O–Mo)
[Mo ₂ O ₄ (acac) ₂ gly](EtOH)(H ₂ O)	3423	3100	1556	1421	964	741
[Mo ₂ O ₄ (acac) ₂ DL-val]	3448	3228	1612	1431	961	743

from the carboxylic group occupy a pair of *trans* sites to Mo=O, and lengthening of these Mo–O bonds is due to the known *trans* effect. Values in **1** and **2** correspond well to these mean values: Mo–O_p distances range from 1.9344(11)° to 1.950(4) Å in **1** and **2**, respectively. The Mo–Mo distances of 2.5678(10) Å in **1**, and 2.5687(2) Å in **2** correspond to a single Mo–Mo bond.^{35,36} The Mo–O_{acac} distances, ranging from 2.086(5) to 2.1038(11) Å, are in good agreement with previously determined similar structures.^{15, 37–40} The Mo–O_{carboxyl} distances fall within the above mentioned range and are from

2.2791(11) to 2.354(4) Å. The overall structures are similar to that of [Mo₂O₄(acac)₂thala]·3EtOH (thala = 3-(2-thienyl)-D,L-alanine).¹⁵ Octahedra around the Mo atoms are significantly distorted with angles ranging from 74.78(4) to 106.58(6). The amino acids in both structures are in the zwitter-ionic form.

3. 2. Crystal Structure of **1**

The asymmetric unit consists of the complex molecule, ethanol and H₂O molecules. The protonated amino

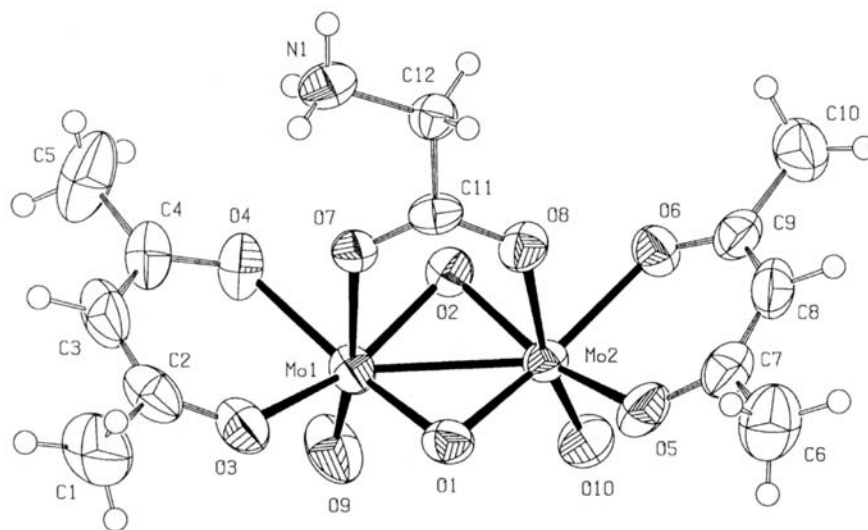


Figure 1. A view of the complex molecule [Mo₂O₄(acac)₂gly] with labeling of the non-hydrogen atoms and with ellipsoids at the 50% probability level.

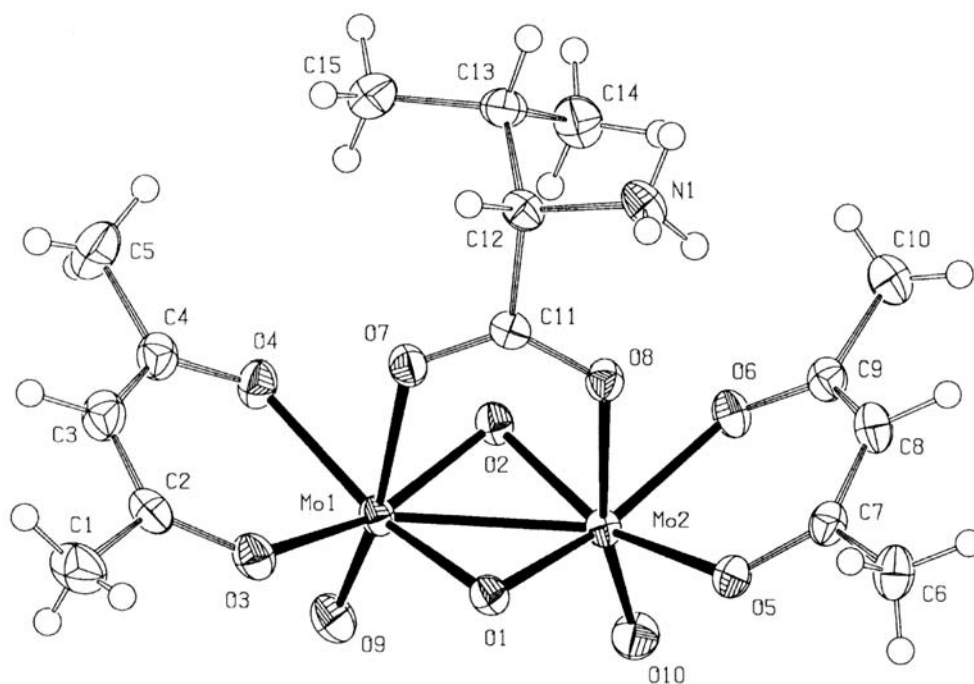
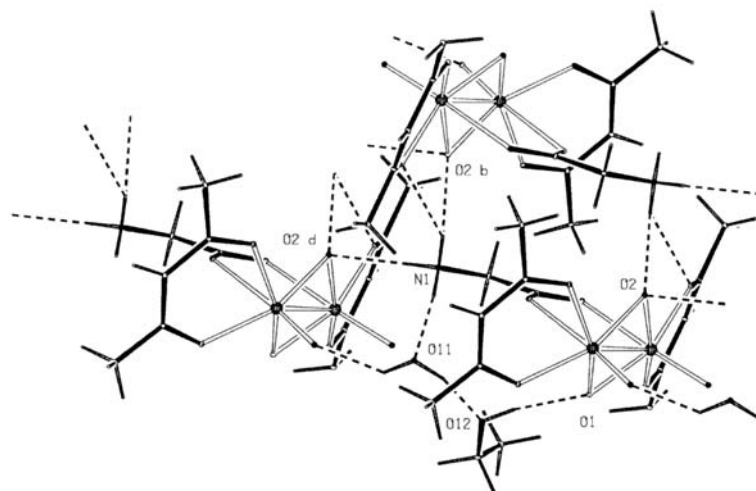


Figure 2. A view of the complex molecule [Mo₂O₄(acac)₂D,L-val], **2**, with labeling of the non-hydrogen atoms and with ellipsoids at the 50% probability level.

Table 3. Selected interatomic distances (Å) and angles (°) in **1** and **2**.

	1	2		1	2
Mo1–Mo2	2.5678(10)	2.5687(2)	O2–Mo1–O3	156.19(18)	157.40(5)
Mo1–O1	1.950(5)	1.9476(11)	O2–Mo1–O4	86.37(18)	85.74(5)
Mo1–O2	1.945(4)	1.9344(11)	O2–Mo1–O7	79.46(16)	80.45(4)
Mo1–O3	2.086(5)	2.0906(12)	O2–Mo2–O5	156.27(18)	156.20(5)
Mo1–O4	2.087(5)	2.0916(12)	O2–Mo2–O6	87.41(18)	84.03(5)
Mo1–O7	2.354(4)	2.3538(12)	O2–Mo2–O8	81.07(17)	82.11(4)
Mo1–O9	1.671(5)	1.6814(12)	O3–Mo1–O4	85.12(19)	85.55(5)
Mo2–O1	1.935(4)	1.9405(11)	O3–Mo1–O7	77.00(17)	77.23(4)
Mo2–O2	1.933(4)	1.9280(11)	O4–Mo1–O7	77.49(18)	76.30(4)
Mo2–O5	2.094(5)	2.0946(11)	O5–Mo2–O6	85.32(19)	85.65(4)
Mo2–O6	2.103(4)	2.1038(11)	O5–Mo2–O8	75.30(18)	74.78(4)
Mo2–O8	2.287(4)	2.2791(11)	O6–Mo2–O8	77.24(17)	77.98(4)
Mo2–O10	1.693(5)	1.6899(12)	O9–Mo1–O2	104.0(2)	105.01(5)
Mo1–O2–Mo2	82.93(16)	83.37(4)	O9–Mo1–O1	103.8(2)	105.41(6)
Mo2–O1–Mo1	82.74(17)	82.70(4)	O9–Mo1–O3	98.9(2)	96.74(5)
O1–Mo1–O3	85.0(2)	84.41(5)	O9–Mo1–O4	95.3(3)	97.09(6)
O1–Mo1–O4	159.70(19)	156.26(5)	O9–Mo1–O7	171.9(2)	171.26(5)
O1–Mo1–O7	83.04(16)	80.53(4)	O10–Mo2–O1	103.2(2)	105.76(5)
O1–Mo2–O2	96.62(18)	95.93(5)	O10–Mo2–O2	105.8(2)	106.58(6)
O1–Mo2–O5	83.4(2)	86.68(4)	O10–Mo2–O5	97.2(2)	95.36(5)
O1–Mo2–O6	160.46(18)	160.11(4)	O10–Mo2–O6	94.0(2)	93.22(5)
O1–Mo2–O8	84.48(17)	82.30(4)	O10–Mo2–O8	168.8(2)	167.11(5)
O2–Mo1–O1	95.73(18)	95.48(5)			

**Figure 3.** Hydrogen bonding in **1** is shown by dashed lines, b: 1-x, -y, 1-z, d: 1+x, y, z.**Table 4.** Hydrogen bonds in **1** and **2**.

	D–H...A	d(D–H) / Å	d(H...A) / Å	d(D...A) / Å	<(DHA) / °
1	N1–H1D...O11	0.89	1.81	2.683(14)	166
	N1–H1E...O2 ⁱ	0.89	2.20	3.078(7)	169
	N1–H1F...O2 ⁱⁱ	0.89	2.41	2.881(7)	114
	N1–H1F...O5 ⁱⁱⁱ	0.89	2.32	3.110(8)	148
	O11–H11A...O9 ⁱ	0.87	1.92	2.648(11)	140
	O11–H11B...O12	0.92	1.54	2.443(17)	165
	O12–H12...O1	0.82	2.00	2.786(13)	160
2	N1–H1...O1 ^{iv}	0.91(2)	1.78(3)	2.6710(19)	166(2)
	N1–H2...O8	0.89(2)	2.15(2)	2.604(2)	110.7(17)
	N1–H3...O6 ^v	0.83(3)	2.25(3)	3.041(2)	161(2)
	N1–H3...O10 ^v	0.83(3)	2.63(3)	3.096(2)	117(2)

i: 1+x, y, z; ii: 1-x, -y, 1-z; iii: 1-x, -y, 1-z; iv: -x, 1-y, 1-z; v: -1/2+x, y, 1/2-z

group is an excellent hydrogen bond donor and all three N1–H atoms are involved in hydrogen bonding, Table 3, Fig. 3. A molecule of $[\text{Mo}_2\text{O}_4(\text{acac})_2\text{gly}]$ is linked to its centrosymmetrically related pair by the hydrogen bonds N1–H1F to O2 and O5, while the hydrogen bond N1–H1E...O2 links it to another neighbouring complex molecule. Through these hydrogen bonds the complex molecules are linked into infinite chains along the *a* axis. The third hydrogen links it with a H_2O molecule, N1–H1D...O11. The H_2O molecule is a donor toward a neighbouring complex molecule through O11–H11A ...O9, and to the ethanol molecule O11–H11B...O1. The ethanol molecule forms another hydrogen bond with a complex

molecule, O12–H12...O1, thus indirectly linking two complex molecules. A packing diagram is shown in Fig. 4.

3.3. Crystal Structure of 2

There are no solvent molecules in 2, however, extensive hydrogen bonding is also found, Table 4, Fig. 5. The protonated amino group is again the hydrogen bond donor through all three hydrogen atoms, however one is intramolecular, N1–H2...O8. A hydrogen bond to the bridging atom of a molecule related by inversion center is formed through N1–H1, while N1–H3 forms two hydrogen bonds with O6 and O10 of another neighbouring molecule. In this way molecules are interlinked in planes parallel to (010), Fig. 6.

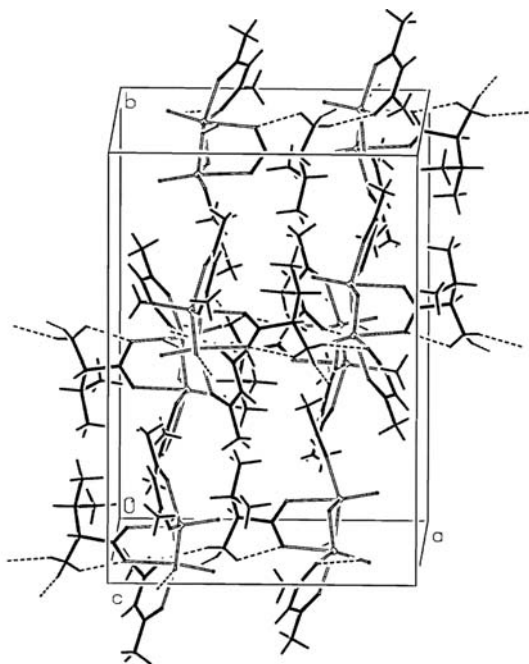


Figure 4. Packing of the molecules of $[\text{Mo}_2\text{O}_4(\text{acac})_2\text{gly}](\text{EtOH})(\text{H}_2\text{O})$, **1**, in the unit cell.

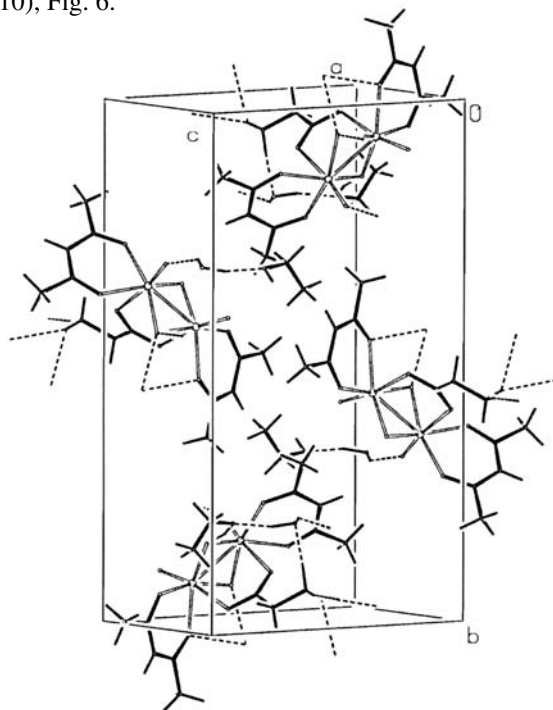


Figure 6. Packing of the molecules of $[\text{Mo}_2\text{O}_4(\text{acac})_2\text{D,L-val}]$, **2**, in the unit cell.

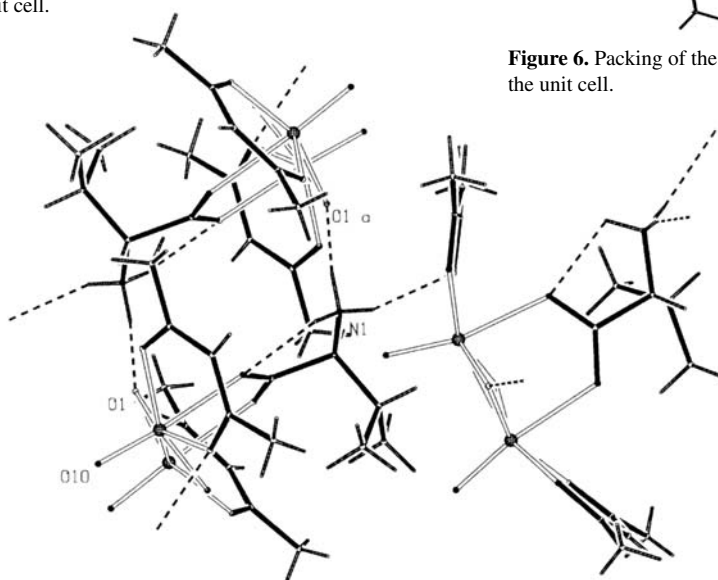


Figure 5. Hydrogen bonding in **2** is shown by dashed lines, a: $-x$, $1-y$, $1-z$. The weak N1–H...O10 hydrogen bond is not shown.

4. Acknowledgement

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Povzetek

Sintetizirali smo dva nova molibden(V) kompleksa, $[\text{Mo}_2\text{O}_4(\text{acac})_2(\text{gly})](\text{EtOH})(\text{H}_2\text{O})$, **1**, in $[\text{Mo}_2\text{O}_4(\text{acac})_2(\text{D,L-val})]$, **2**, (acac = acetilacetono, EtOH = etanol), z reakcijo med $[\text{Mo}_2\text{O}_3(\text{acac})_4]$ in amino kislinama glicin and D,L-valin. Komplekse smo okarakterizirali z elementno in IR spektralno analizo. Strukturi smo določili z rentgensko difrakcijo na monokristalu. Oba kompleksa sta dinuklearna z enojno vezanim Mo–Mo v $\{\text{Mo}_2\text{O}_4\}^{2+}$, z amino kislino vezano preko karboksilata ter z vsakim Mo atomom dodatno koordiniranim z bidentatnim acetilacetono ligandom. Kristalografski podatki: $\text{C}_{14}\text{H}_{27}\text{Mo}_2\text{NO}_{12}$ (**1**) kristalizira v monoklinskem sistemu, prostorska skupina $P2_1/n$, $a = 8.439(2)$, $b = 20.613(4)$, $c = 12.639(3)$ Å, $\beta = 98.410(10)^\circ$, $Z = 4$; $\text{C}_{15}\text{H}_{25}\text{Mo}_2\text{NO}_{10}$ (**2**) kristalizira v ortorombičnem sistemu, prostorska skupina $Pbca$, $a = 13.596(1)$, $b = 19.346(1)$, $c = 15.080(1)$ Å, $Z = 8$.