

Scientific paper

New Molybdenum(VI) Complexes with Thiosemicarbazone Ligands Containing 4-hydroxy-2-pyrone Ring

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Dedicated to the memory of Professor Ljubo Golič

Abstract

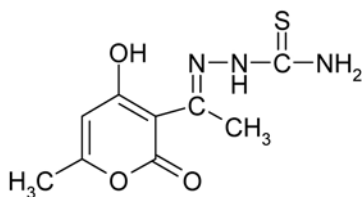
New molybdenum(VI) complexes have been prepared by the reaction of $[\text{MoO}_2(\text{acac})_2]$ (acac = acetylacetonate ion) with the thiosemicarbazone ligands derived from dehydroacetic acid and thiosemicarbazide (H_2L^1) or 4-phenylthiosemicarbazide (H_2L^2). All complexes consist of the MoO_2^{2+} core with molybdenum coordinated by ligand L via three donor atoms: pyran-4-ol-oxygen, imine-nitrogen and thiol-sulphur. Unlike the monomeric complexes $[\text{MoO}_2\text{L}^2\text{D}]$, where the octahedral coordination around the molybdenum atom is achieved by additional coordination of one neutral solvent molecule D (methanol in **2a** or ethanol in **2b**), in the polymeric complexes $[\text{MoO}_2\text{L}]_n$ (**1** and **2**) the octahedral coordination is accomplished by an intermolecular metal-oxygen interaction (metal...oxygen//Mo=O...Mo=O). All compounds were characterized by means of elemental analyses, IR spectra, thermal analysis and some of them by X-ray crystallography (ligand HL^1 and complex **2b**).

Keywords: Molybdenum(VI) complexes; dehydroacetic acid, thiosemicarbazone; pyrone; crystal structure

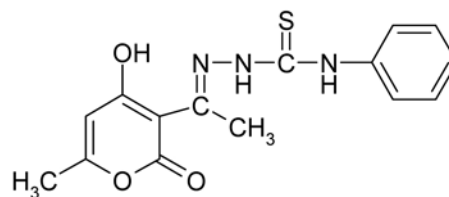
1. Introduction

Various biological activities (including antibacterial, antiviral and antitumor activities) of thiosemicarbazones and their metal complexes have inspired numerous investigations concerning their syntheses, characterization and bioinorganic relevance.^{1–5} 2-Pyrone derivatives and their metal complexes have received similar attention in

chemistry and biology.^{6–10} However, little is known about complexes with thiosemicarbazone ligands containing the 2-pyrone ring.^{11–14} As far as we know only the copper(II) complex $[\text{Cu}(\text{DAhexim-H})\text{Cl}] \cdot \text{MeCN}$ (DAhexim-H = 3-hexamethyleneiminyl-N-substituted thiosemicarbazone of dehydroacetic acid) has been structurally characterized.¹¹



H_2L^1



H_2L^2

Scheme 1

Due to the biological properties of such compounds we are interested in nature of coordination as well as in the structural and spectral properties of molybdenum complexes with thiosemicarbazone ligands. Recently we have published syntheses and structures of several molybdenum(VI) complexes with aromatic thiosemicarbazones (salicylaldehyde, 2-hydroxy-1-naphthaldehyde, 2-hydroxy-3-methoxybenzaldehyde or 4-(diethylamino)salicylaldehyde).^{15–18} Continuing with our research on thiosemicarbazones, we report here the synthesis of novel molybdenum(VI) complexes $[\text{MoO}_2\text{L}]_n$ (**1** and **2**), $[\text{MoO}_2\text{LD}]$, (**2a**, D = methanol and **2b**, D = ethanol) with thiosemicarbazone ligands containing 4-hydroxy-2-pyrene ring derived from dehydroacetic acid (Scheme 1). The molecular structures of molybdenum(VI) complex (**2b**), as well as of one ligand (H_2L^1) have been determined by a single crystal X-ray diffraction method.

The ligands and complexes have also been characterized by means of chemical analyses, thermal analysis and IR spectroscopy.

2. Experimental

All chemicals were of reagent grade and used as purchased. The starting complex $[\text{MoO}_2(\text{acac})_2]$ was prepared as described in the literature.¹⁹ Methanol and ethanol were dried using magnesium turnings and iodine, and then distilled. Acetonitrile was dried over P_2O_5 . C, H, N and S analyses were provided by the Analytical Services Laboratory of Rudjer Bošković Institute, Zagreb. Infrared spectra were recorded in KBr with an FTIR 1600, Fourier transform spectrophotometer in the 4500–450 cm^{-1} region. Thermogravimetric (TG) analyses were measured on a Mettler TG 50 thermobalance using aluminum crucibles under oxygen atmosphere with the temperature range from 25 to 600 °C. Melting points of the H_2L^1 and H_2L^2 were determined using differential scanning calorimetry on a Mettler DSC 30 instrument under nitrogen atmosphere with the temperature range from 25 to 250 °C. All experiments were recorded with a heating rate of 5 °C min^{-1} in a dynamic atmosphere with a flow rate of 200 $\text{cm}^3 \text{min}^{-1}$. The results were developed by applying the Mettler STAR[®] 6.1. programme.

2. 1. Synthesis of Thiosemicarbazones (H_2L^1 , H_2L^2)

Thiosemicarbazones H_2L^1 and H_2L^2 (Scheme 1) were prepared by the reaction of dehydroacetic acid (dha = 3-acetyl-4-hydroxy-6-methyl-2H-pyran-2-one) and appropriate thiosemicarbazides $\text{H}_2\text{NNHC(S)NHR}$ (where R = H, or C_6H_5) according to already described procedure.²⁰ From the DSC measurements it follows that the melting points for ligands were 196 °C and 184 °C for H_2L^1 and H_2L^2 , respectively. Single crystals of H_2L^1 suitable for the

X-ray diffraction study were obtained by recrystallization of H_2L^1 from ethanol.

2. 2. Synthesis of Thiosemicarbazone Complexes

2. 2. 1. Synthesis of $[\text{MoO}_2\text{L}^1]_n$ (**1**)

$[\text{MoO}_2(\text{acac})_2]$ (0.1 g, 0.3 mmol) was dissolved in dry acetonitrile (20 mL) and H_2L^1 (0.3 mmol) was added. The mixture was refluxed for 12 h and a greenish brown product deposited during warming of the reaction mixture. It was filtered off, washed with acetonitrile, methanol and dried.

Yield: 0.03 g, 27%. Found: C, 29.04; H, 2.23; N, 11.13; S, 8.25%. Anal. Calcd. for $\text{C}_9\text{H}_9\text{MoN}_3\text{O}_5\text{S}$: C, 29.44; H, 2.47; N, 11.44; S, 8.73%. TG: 38.85% MoO_3 (Calcd. 39.20%)

Selected IR data (cm^{-1}): 1717 (C=O), 1640 (C=O), 1559 (C=N), 1507 (C–O), 905 (MoO_2), 829 ($\text{Mo}=\text{O}\cdots\text{Mo}$), 752 (C–S).

2. 2. 2. Synthesis of $[\text{MoO}_2\text{L}^2]_n$ (**2**)

$[\text{MoO}_2(\text{acac})_2]$ (0.1 g, 0.3 mmol) was dissolved in dry acetonitrile (20 mL) and H_2L^2 (0.3 mmol) was added. The mixture was refluxed for 6 h and a greenish brown product deposited during warming of the reaction mixture. It was filtered off, washed with acetonitrile and dried.

(**2**) Yield: 0.11 g, 81%. Found: C, 40.11; H, 2.50; N, 9.21; S, 7.05%. Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{MoN}_3\text{O}_5\text{S}$: C, 40.64; H, 2.96; N, 9.48; S, 7.23%. TG: 31.93% MoO_3 (Calcd. 32.47%)

Selected IR data (cm^{-1}): 1700 (C=O), 1645 (C=O), 1568 (C=N), 1528 (C–O), 918 (MoO_2), 827 ($\text{Mo}=\text{O}\cdots\text{Mo}$), 759 (C–S).

2. 2. 3. Synthesis of $[\text{MoO}_2\text{L}^2(\text{ROH})]$ (**2a**, **2b**)

$[\text{MoO}_2(\text{acac})_2]$ (0.15 g, 0.46 mmol) was dissolved in dry alcohol (30 mL) and H_2L^2 (0.46 mmol) was added. The mixture was warmed up for 5 h, the solution was evaporated to one third of its volume under reduced pressure and left at room temperature. Upon standing for a few days the red crystalline products were filtered off and dried.

$[\text{MoO}_2\text{L}^2(\text{CH}_3\text{OH})]$ (**2a**) Red needle shaped crystals of **2a** obtained from the methanol solution were readily losing solvated methanol molecules at room temperature. They were left in a dessicator up to constant weight and analyzed as unsolvated species.

Yield: 0.04 g, 81%. Found: C, 40.11; H, 2.50; N, 9.21; S, 7.05%. Anal. Calcd. for $\text{C}_{16}\text{H}_{17}\text{MoN}_3\text{O}_6\text{S}$: C, 40.43; H, 3.60; N, 8.84; S, 6.75%. TG: 29.93% MoO_3 (Calcd. 30.28%), 7.04% CH_3OH (Calcd. 6.74%).

Selected IR data (cm^{-1}): 1699 (C=O), 1636 (C=O), 1567 (C=N), 1520 (C–O), 934 ($\text{MoO}_{2\text{-asym}}$), 889 ($\text{MoO}_{2\text{-sym}}$), 754 (C–S).

$[MoO_2L^2(CH_3CH_2OH)]$ (**2b**) Red plate like crystals. Yield: 0.06 g, 81%. Found: C, 40.64; H, 2.96; N, 9.48; S, 7.23%. Anal. Calcd. for $C_{17}H_{19}MoN_3O_6S$: C, 41.72; H, 3.91; N, 8.59; S, 6.55%. $C_{17}H_{19}O_6S$: C, 40.64; H, 2.96; N, 9.48; S, 7.23%. TG: 28.87% MoO_3 (Calcd. 29.42%); 9.22% C_2H_5OH (Calcd. 9.41%)

Selected IR data (cm^{-1}): 1694 (C=O), 1637 (C=O), 1569 (C=N), 1521 (C–O), 942 (MoO_{2-asym}), 902 (MoO_{2-sym}), 758 (C–S).

2. 3. X-ray Crystallography

Crystals of H_2L^1 were stable and diffraction data could be collected at room temperature. On contrary, crystals of **2b** were unstable upon prolonged exposure to air. Room temperature data of **2b** crystal in a capillary was extremely poor. A crystal protected with vacuum grease at low temperature still decomposed so the method of protein crystal mounting was adapted for the second data collection. The crystal was mounted in a loop in a mixture of ethanol and glycerol, and cooled in nitrogen vapor stream at 110 K. Diffraction intensity data for both compounds, H_2L^1 and **2b** were collected by ω -scans on an Oxford Diffraction Xcalibur CCD diffractometer with graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and reduced using the CRYALIS software package.²¹ Analytical absorption correction gave no improvement of the **2b** data set. The data for **2b** is not of

best quality because of slight decomposition of the crystal.

Solution, refinement and analysis of the structures were done using the programs integrated in the WINGX system.²² The structures were solved by direct methods using the SHELXS97 program.²³ The refinement procedure by the full-matrix least-squares method based on F^2 against all reflections included anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were placed in calculated positions. Refinement was performed using the SHELXL97 program.²⁴ Geometrical calculations and the figures were performed using the PLATON program.²⁵ Crystal data, experimental conditions and refinement parameters are summarized in Table 1.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary material with the deposition numbers CCDC 682 602 and CCDC 682 603. Copies of the data can be obtained, free of charge via <http://www.ccdc.cam.ac.uk/const/retrieving.html>.

3. Results and Discussion

The complexes are prepared by the reaction of $[MoO_2(acac)_2]$ (acac = acetylacetonate ion) with the thiosemicarbazone ligands derived from dehydroacetic acid (dha)

Table 1. Crystallographic data for compounds H_2L^1 and **2b**.

Compound	H_2L^1	2b
Empirical formula	$C_9H_{11}N_3O_3S$	$C_{17}H_{19}MoN_3O_6S$
Formula weight	241.27	489.35
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (\AA)	7.885(2)	8.531(5)
b (\AA)	12.201(3)	10.157(7)
c (\AA)	11.679(3)	11.564(5)
α ($^\circ$)	90	97.540(5)
β ($^\circ$)	102.84(2)	104.300(5)
γ ($^\circ$)	90	91.120(5)
V (\AA^3)	1095.5(5)	961.2(10)
Z	4	2
T (K)	295(2)	110(2)
D_{calc} ($g\ cm^{-3}$)	1.463	1.687
μ ($MoK\alpha$) (mm^{-1})	0.292	0.831
$F(000)$	504	496
Ranges of h, k, l	–9–9, –14–14, –13–13	–10–9, –12–12, –13–11
Reflections collected/ unique / observed $I > 2.0 \sigma(I)$	5966/1916/1685	6543/3347/2538
Data/restraints/parameters	1916/0/189	3347/0/253
Goodness of fit on F^2	1.11	1.07
R^a & wR^b	0.0403, 0.1108	0.0854, 0.1924
(Shift/s.u.) _{max}	<0.001	<0.001
Largest diff. peak & hole/ ($e\ \text{\AA}^{-3}$)	0.15, –0.22	1.19, –1.09

^a $R = \sum |F_o| - |F_c| / \sum |F_o|$

^b $wR = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

and thiosemicarbazide (H_2L^1) or 4-phenylthiosemicarbazide (H_2L^2). If the reaction is carried out using acetonitrile as solvent the polymeric greenish brown complex $[\text{MoO}_2\text{L}]_n$ is obtained. The monomeric red coloured complexes $[\text{MoO}_2\text{L}^2\text{D}]$ containing methanol (**2a**) or ethanol (**2b**) as the additional ligand are obtained only from the reactions of H_2L^2 with $[\text{MoO}_2(\text{acac})_2]$ using the appropriate alcohol as solvent. From the analogous reaction with H_2L^1 we were not able to isolate the monomeric complex suggesting that the polymeric chains $\text{Mo}=\text{O}\cdots\text{Mo}=\text{O}\cdots$ are not easily cleaved by donor solvents like methanol or ethanol. The brown and red colours of the compounds are typical for the thiosemicarbazonato polymeric and monomeric molybdenum(VI) complexes, respectively. The electronic spectra of similar thiosemicarbazonato complexes are well-known in the literature.^{26–28}

All complexes consist of the MoO_2^{2+} core coordinated by ligand L *via* three donor atoms, pyran-4-ol-oxygen, imine-nitrogen and thiol-sulphur. The octahedral coordination around the molybdenum atoms is completed by the neutral solvent molecule D in $[\text{MoO}_2\text{L}^2\text{D}]$ (**2a**, D = methanol and **2b**, D = ethanol) or by an intermolecular metaloxygen interaction (metal...oxygen $\text{Mo}=\text{O}\cdots\text{Mo}=\text{O}$) in $[\text{MoO}_2\text{L}]_n$ (**1** and **2**).

The IR spectra support such structures. The single strong absorption attributed to $\text{Mo}=\text{O}$ at 905 cm^{-1} (**1**) or 918 cm^{-1} (**2**), accompanied with a broad band at 827 cm^{-1} (**1**) or 829 cm^{-1} (**2**) is indicative for the $\text{Mo}=\text{O}\cdots\text{Mo}=\text{O}\cdots$ interaction, which is in agreement with literature values. The structure of the $[\text{MoO}_2\text{L}]_n$ complexes *via* such interactions in some cases is confirmed also by X-ray method.^{29,30} The main characteristic of the IR spectra of the monomeric complexes is appearance of $\nu_{\text{asym}}(\text{MoO}_2)$ at 934 cm^{-1} (for **2a**) and 942 cm^{-1} (for **2b**), $\nu_{\text{sym}}(\text{MoO}_2)$ at 889 cm^{-1} (for **2a**) and 902 cm^{-1} (for **2b**), together with absence of the broad band indicative for the $\text{Mo}=\text{O}\cdots\text{Mo}$ bridging. The stretching frequencies attributed to coordinated groups are found at about 1560 cm^{-1} (for $\text{C}-\text{O}_{\text{pyran-4-ol-oxygen}}$), 1520 cm^{-1} (for $\text{C}=\text{N}$) and 750 cm^{-1} (for $\text{C}-\text{S}$). Two bands at $1717\text{--}1694\text{ cm}^{-1}$ and $1645\text{--}1636\text{ cm}^{-1}$ are assigned to the stretching vi-

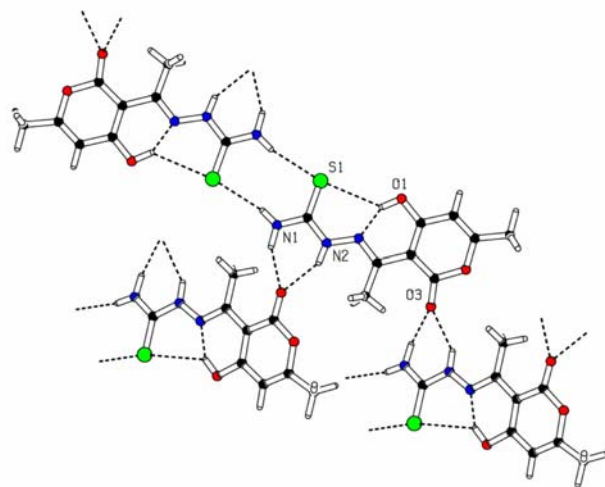


Fig. 2: Hydrogen bonding in the crystal structure of the ligand H_2L^1

brations of the carbonyl group from the ester COOC_2H_5 and 2-pyrone, respectively. The remaining frequencies in the IR spectra are due to the vibrations within the ligand.

The monomeric complexes $[\text{MoO}_2\text{L}^2(\text{CH}_3\text{OH})]$ (**2a**) and $[\text{MoO}_2\text{L}^2(\text{CH}_3\text{CH}_2\text{OH})]$ (**2b**) show similar thermal behaviour. While heated the first weight loss is attributed to the loss of the coordinated alcohol molecule and conversion into a stable species $[\text{MoO}_2\text{L}^2]$. On further heating, significant weight losses are indicative of complex decomposition resulting in the solid residue identified as MoO_3 . The weight losses of the polymeric complexes $[\text{MoO}_2\text{L}]_n$ (**1**) and $[\text{MoO}_2\text{L}^2]_n$ (**2**) correspond to the decomposition resulting in the formation of the MoO_3 . The agreement between theoretical and experimental mass losses is within the experimental error.

3. 1. X-ray Crystallography

Comparison of the selected bond distances for H_2L^1 and **2b** is given in Table 2. Hydrogen-bonding parameters are listed in Table 3.

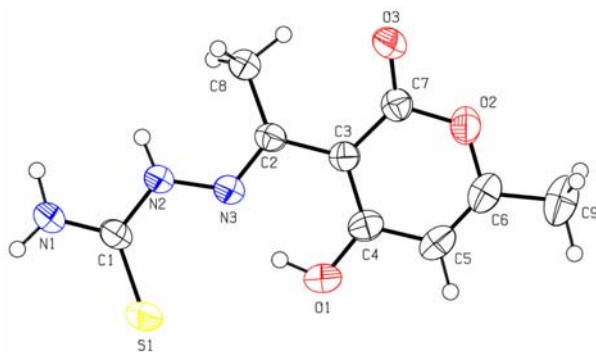


Fig. 1: ORTEP plot of the ligand molecule H_2L^1 with the atom labelling scheme. Ellipsoids are drawn at the 50% probability level.

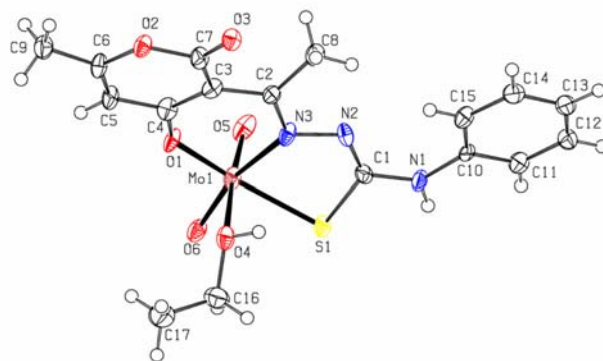


Fig. 3: ORTEP plot of the complex molecule **2b** with the atom labelling scheme. Ellipsoids are drawn at the 50% probability level.

Table 2. Selected bond distances (Å) and angles (°) for **H₂L¹** and **2b**.

	H₂L¹	2b
S1–C1	1.673(2)	1.780(8)
N1–C1	1.324(3)	1.354(10)
C1–N2	1.350(2)	1.298(11)
N2–N3	1.364(2)	1.391(9)
N3–C2	1.286(2)	1.336(12)
C2–C3	1.465(2)	1.481(11)
C2–C8	1.493(3)	1.507(12)
C3–C4	1.397(2)	1.388(11)
C3–C7	1.425(2)	1.439(12)
C7–O3	1.217(2)	1.226(9)
C4–O1	1.309(2)	1.325(11)
Mo1–S1		2.432(3)
Mo1–O1		1.974(6)
Mo1–O4		2.349(6)
Mo1–O5		1.706(7)
Mo1–O6		1.702(6)
Mo1–N3		2.295(6)
N1–C1–N2	113.65(18)	121.0(7)
S1–C1–N1	123.45(16)	112.6(6)
N3–C2–C3	121.89(16)	121.3(7)
N3–C2–C8	121.89(16)	119.4(7)
O5–Mo1–O6		105.4(3)
S1–Mo1–O1	153.91(15)	
S1–Mo1–O4		81.25(14)
S1–Mo1–O5		97.0(2)
S1–Mo1–O6		92.9(2)
S1–Mo1–N3		76.83(17)
O1–Mo1–O4		79.5(2)
O1–Mo1–O5		98.9(3)
O1–Mo1–O6		102.6(3)
O1–Mo1–N3		81.7(2)
O4–Mo1–O5		169.9(2)
O4–Mo1–O6		84.8(3)
O4–Mo1–N3		76.7(2)
O5–Mo1–N3		93.3(3)
O6–Mo1–N3		159.7(3)

ORTEP plot of **H₂L¹** is shown in Fig. 1. The ligand molecule **H₂L¹** is found to be in the keto tautomeric form with the distances C1–S1 of 1.673(2) Å and N2–C1 of 1.350(2) Å. It consists of two nearly planar fragments connected by a single C2–C3 bond: first fragment (S1, N1, N2, N3, C1, C2, C3, C8) and second fragment (O1, C4, C3, C7, O3, O2, C6, C5, C9). Dihedral angle between the

two planes is 11.38(7)°. The C4 atom is in the *syn* conformation in respect to the N3 atom (torsion angle C4–C3–C2–N3=10.0(2)°) stabilized by an intramolecular O1–H···N3 hydrogen bond. In the crystal structure of **H₂L¹** molecules are interconnected by two strong N1–H···O3 [2–x, –1/2+y, 3/2–z] hydrogen bonds and one N1–H···S1 [1–x, –y, 1–z] hydrogen bond (Fig. 2).

Complex molecule found in the crystal structure of **2b** is shown in Fig. 3. The molybdenum atom in this complex has a distorted octahedral coordination. Molecule **2b** consists of the *cis*-[MoO₂]²⁺ moiety, with the tridentate thiosemicarbazone ligand bonded to molybdenum through the phenolic-oxygen, imine-nitrogen and thiolato-sulphur atoms. The sixth coordination site is occupied by an oxygen atom from the ethanol molecule. The ligand in the complex is bonded in its enethiol form indicated by the bond distances N2–C1 [1.295(11) Å] and C1S1 [1.781 (8) Å]. The Mo=O bond lengths [1.702(6) and 1.706(7) Å] and the O=Mo=O [105.4(3)°] bond angle are similar to those found in *cis*-dioxomolybdenum(VI) complexes. The bond distances Mo1–S1 [2.432(3) Å], Mo1–O1 [1.974(6) Å], Mo1–N3 [2.295(6) Å] are similar to those found in other thiosemicarbazonato molybdenum(VI) complexes.^{15,16,18} The bond distance Mo1–O4 [2.349(6) Å] is significantly larger in comparison to Mo–O1. In the crystal structure of **2b** molecules are bonded by two hydrogen bonds O4–H4···O3 [2–x, 1–y, –z] and N1–H1···S1 [1–x, 1–y, –z].

4. Conclusions

New thiosemicarbazonato molybdenum(VI) complexes consist of the MoO₂²⁺ core coordinated by tridentate ONS donor ligand through pyran-4-ol-oxygen, imine-nitrogen and thiol-sulphur. The octahedral coordination of each molybdenum atom is completed either by one neutral solvent molecule D in [MoO₂L²D] (methanol or ethanol) or by the oxygen atom of M=O unit from the neighbouring molecule.

5. Acknowledgements

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Table 3. Hydrogen bonding geometry in structures **H₂L¹** and **2b**.

	D–H···A	d(D–H) / Å	d(H···A) / Å	d(D···A) / Å	<(DHA) / °
H₂L¹	N1–H1NA···O3 [2–x, –1/2+y, 3/2–z]	0.94(2)	2.10(3)	2.896(3)	142(2)
	N1–H1NB···S1 [1–x, –y, 1–z]	0.86(2)	2.53(2)	3.368(2)	164(2)
	N2–H2N···O3 [2–x, –1/2+y, 3/2–z]	0.87(2)	2.11(2)	2.876(2)	146(2)
	O1–H1O···S1	0.91(3)	2.84(4)	3.5284(19)	134(2)
	O1–H1O···N3	0.91(3)	1.67(3)	2.489(2)	149(3)
2b	N1–H1···S1 [1–x, –y, –z]	0.8600	2.6700	3.475(8)	157.00
	O4–H4···O3 [2–x, 1–y, –z]	0.8600	1.9000	2.711(7)	157.00

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Povzetek

Z reakcijo med $[\text{MoO}_2(\text{acac})_2]$ (acac = acetilacetonatni ion) z tiosemikarbazonom iz dehidroocetne kisline in tiosemikarbazida (H_2L^1) ali iz 4-feniltiosemikarbazida (H_2L^2) so bili pripravljene novi molibdenovi(VI) kompleksi. Osnova v vseh kompleksih je jedro MoO_2^{2+} . Molibdenov atom je koordiniran z ligandom L preko treh donorskih atomov: kisika v piran-4-olu, iminskega dušika in tiolnega žvepla. Vse spojine so bile okarakterizirane z elementno analizo, z IR spektri, s termično analizo in nekatere tudi z rentgenskimi kristalografskimi metodami.