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Synthesis of five new molybdenum(VI) thiosemicarbazonato complexes. Crystal structures of salicylaldehyde and 3-methoxy-salicylaldehyde 4-methylthiosemicarbazones and their molybdenum(VI) complexes

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Abstract

Polynuclear $[MoO_2\{SalTSC\text{-}4\text{-}Me\}]_n$ (**I**), $[MoO_2\{VanTSC\text{-}4\text{-}Me\}]_n$ (**II**) and mononuclear $[MoO_2\{SalTSC\text{-}4\text{-}Me\}(CH_3OH)]$ (**1a**), $[MoO_2\{VanTSC\text{-}4\text{-}Me\}(CH_3OH)]$ (**2a**) and $[MoO_2\{VanTSC\text{-}4\text{-}Me\}(H_2O)]\cdot CH_3CN$ (**2b**) complexes have been prepared by the reaction of the $[MoO_2(acac)_2]$ (acetylacetonate ligand, $acac^-$, $C_5H_7O_2^-$) with **1** (salicylaldehyde 4-methylthiosemicarbazone ligand, $C_6H_4(OH)CH{:}NNC(SH)NHCH_3H_2SalTSC\text{-}4\text{-}Me$) or **2** (3-methoxy-salicylaldehyde 4-methylthiosemicarbazone, $CH_3OC_6H_3(OH)\text{-}CH{:}NNC(SH)NHCH_3$, $H_2VanTSC\text{-}4\text{-}Me$) in acetonitrile or in dry methanol. All complexes have been characterized by means of chemical analyses, thermogravimetric analyses, IR spectroscopy and some of them by ^1H, ^{13}C NMR spectroscopy and X-ray crystallography. In all mononuclear complexes molybdenum atom is coordinated by two terminal oxo-oxygen atoms, by ONS atoms from the ligand molecule and by an oxygen atom from methanol (in **1a** and **2a**) or water (in **2b**) molecules. Ligands **1** and **2** have been characterized by means of ^1H, ^{13}C NMR spectroscopy and X-ray crystallography. Molecules of both ligands are found to be in the thioketo tautomeric form.

Keywords: Molybdenum(VI) complexes; Thiosemicarbazones; Mononuclear and polynuclear complexes; Tridentate ligands; Crystal structures

1. Introduction

In this paper we present a study of five new molybdenum(VI) complexes in which molybdenum atoms are coordinated by salicylaldehyde and 3-methoxysalicylaldehyde 4-methylthiosemicarbazones as ONS ligands. The structure of both ligands as well as of three complexes have been characterized by X-ray crystallography.

Our interest in studies of molybdenum(VI) complexes containing ligands with oxygen, nitrogen and sulfur donor atoms arises from their significant antifungal, antiprotozoal, antibacterial and anticancer activity [1,2]. Similarly, the thiosemicarbazone ligands and related metal complexes have experienced long standing applications in biology and medicine [3,4] as well as in the catalysis of chemical and petrochemical processes [5,6]. The thiosemicarbazones and their complexes showed lower antibacterial activity than thiosemicarbazides [7]. This may be correlated with the

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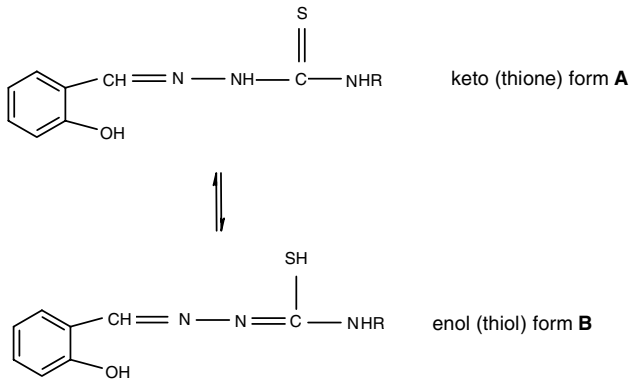


Scheme 1.

decrease of negative charge at the substituted N hydrazinic atom [8].

The thiosemicarbazone ligands can act as tridentate ligands (**A** form) being coordinated through the deprotonated phenolic O, imino N and thiocarbonyl S, or as doubly negatively charged tridentate ligands by losing another proton from the tautomeric mercapto group (**B** form) (Scheme 1) [8].

The biological activity, particularly antitumour activity of this class of compounds is most probably associated with their structures [9–11] as it was found for thiosemicarbazone copper(II) complexes.

2. Experimental

The starting complex $[MoO_2(acac)_2]$ [12], salicylaldehyde and 3-methoxysalicylaldehyde 4-methylthiosemicarbazone were prepared as described in the literature [7]. Acetonitrile was of reagent grade and used as purchased. Methanol was dried over magnesium ethoxide.

C, H and N analyses were provided by the Analytical Services Laboratory of Rudjer Bošković Institute, Zagreb. Molybdenum was determined according to the already known method [13]. Infrared spectra were recorded in KBr with an FTIR 1600 Fourier transform spectrophotometer in the 4500–450 cm^{-1} region. Thermogravimetric analyses were measured on a Mettler TG 50 thermobalance using aluminum crucibles under oxygen atmosphere with a heating rate of 5 °C min^{-1}. For all experiments the temperature ranged from 25 to 600 °C. The results were developed by applying the Mettler STAR^e 6.1. programme.

2.1. Syntheses of molybdenum(VI) complexes: *I, II, 1a, 2a, 2b*

A mixture of $[MoO_2(C_5H_7O_2)_2]$ (0.30 g, 0.92 mmol) and salicylaldehyde 4-methylthiosemicarbazone (0.19 g, 0.92 mmol) for **I** (or 3-methoxysalicylaldehyde 4-methylthiosemicarbazone 0.22 g, 0.92 mmol for **II)** in acetonitrile (40 cm^3) was refluxed for 6 h for **I** and 20 h for **II**, respectively. The brown products **I** or **II** were deposited during refluxing of the reaction mixture and filtered off. The orange crystals **2b** were obtained from the filtrate when it was left at room temperature for two weeks.

(**I**) Yield: 0.23 g, 74.58%. *Anal.* Calc. for $C_9H_9MoN_3O_3S$: C, 32.3; H, 2.7; Mo, 28.6; N, 12.5; S, 9.6. Found: C, 32.0; H, 2.6; Mo, 28.4; N, 12.4; S, 9.8%.

IR (cm^{-1}): 3428(s), 1606(s), 1595(m), 1560(s), 1541(s), 1498(s), 920(vs), 843(s), 806(vs), 765(vs).

(**II**) Yield: 0.20 g, 59.5%. *Anal.* Calc. for $C_{10}H_{11}MoN_3O_4S$: C, 42.7; H, 2.7; Mo, 26.3; N, 11.5; S, 8.8. Found: C, 42.6; H, 2.6; Mo, 26.4; N, 11.4; S, 8.6%.

IR (cm^{-1}): 3409(s), 3342(m), 3309(m), 1568(s), 1545(s), 1273(vs), 923(s), 808(vs).

(**2b**) Yield: 0.01 g, 2.7%. *Anal.* Calc. for $C_{12}H_{16}MoN_4O_5S$: C, 42.4; H, 3.6; Mo, 22.6; N, 13.2; S, 7.6. Found: C, 42.1; H, 3.5; Mo, 22.8; N, 13.1; S, 7.6%.

IR (cm^{-1}): 3376(s), 1593(s), 1565(s), 1525(s), 1412(s), 1259(s), 933(s), 891(vs).

The methanolic solution (15 cm^3) of **I** (0.10 g) or **II** (0.10 g) was refluxed for 4 h and was then evaporated to one-third of its volume. Upon standing at room temperature for few days the orange crystals of **1a** (or **2a**) were obtained and filtered off.

(**1a**) Yield: 0.08 g, 23.7%. *Anal.* Calc. for $C_{10}H_{12}MoN_3O_4S$: C, 32.7; H, 3.3; Mo, 26.1; N, 11.4; S, 8.7. Found: C, 32.8; H, 3.5; Mo, 26.0; N, 11.2; S, 9.0%.

IR (cm^{-1}): 3315(m), 1606(s), 1559(s), 1526(s), 1412(s), 1288(s), 1013(vs), 932(s), 890(vs), 758(vs).

(**2a**) Yield: 0.05 g, 13.8%. *Anal.* Calc. for $C_{11}H_{15}MoN_3O_5S$: C, 42.3; H, 3.6; Mo, 24.2; N, 10.6; S, 8.1. Found: C, 42.5; H, 3.5; Mo, 24.5; N, 10.4; S, 8.4%.

IR (cm^{-1}): 3332(s), 1602(s), 1568(s), 1538(vs), 1467(s), 1438(s), 1293(s), 1258(vs), 934(vs), 889(vs).

2.2. X-ray crystallography

Diffraction intensity data for **1**, **1a**, **2**, **2a** and **2b** were collected by ω-scans on Oxford Diffraction Xcalibur CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and reduced using the CRYSALIS software package [14]. Crystal data, experimental conditions and final refinement parameters are summarized in Table 1. The structures were solved using SHELXS97 [15]: the structures of ligands **1** and **2** by direct methods, and the structures of complexes **1a**, **2a** and **2b** by the Patterson method. 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 located in the difference Fourier maps. Those with poor geometry were then refined with restraints. Hydrogen atoms in **1** and **2** were refined isotropically except the methyl H atoms in both structures for which only the torsion angles and grouped isotropic temperature

Table 1
Crystallographic data for compounds **1**, **1a**, **2**, **2a** and **2b**

Compound	**1**	**1a**	**2**	**2a**	**2b**
Chemical formula	$C_9H_{11}N_3OS$	$[MoO_2(C_9H_9N_3OS)(CH_3OH)]$	$C_{10}H_{13}N_3O_2S$	$[MoO_2(C_{10}H_{11}N_3O_2S)(CH_3OH)]$	$[MoO_2(C_{10}H_{11}N_3O_2S)(H_2O)] \cdot CH_3CN$
M_r	209.27	367.23	239.29	397.26	424.29
Crystal colour, habit	colourless, plate	orange, needle	colourless, needle	orange, needle	orange-red, prismatic
Crystal size (mm)	$0.12 \times 0.77 \times 0.84$	$0.06 \times 0.07 \times 0.59$	$0.05 \times 0.09 \times 0.34$	$0.10 \times 0.18 \times 0.68$	$0.15 \times 0.18 \times 0.42$
Crystal system	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$Pna2_1$	$P2_1/c$	$P2_1/n$	$P2_1/c$
Unit cell dimensions					
a (Å)	6.0270(10)	20.635(3)	11.699(2)	21.2125(10)	7.4539(5)
b (Å)	8.5276(11)	7.1710(10)	6.0149(10)	6.9469(4)	16.4922(12)
c (Å)	10.4743(13)	17.832(2)	16.048(3)	21.2189(13)	13.2293(10)
α (°)	75.724(11)	90	90	90	90
β (°)	75.802(13)	90	102.234(18)	108.105(5)	104.995(6)
γ (°)	82.155(12)	90	90	90	90
V (Å^3)	504.12(13)	2638.7(6)	1103.6(3)	2972.0(3)	1570.9(2)
Z	2	8	4	8	4
T (K)	295(2)	295(2)	100(1)	100(1)	100(1)
D_{calc} (g cm^{-3})	1.379	1.849	1.440	1.776	1.794
μ(Mo Kα) (mm^{-1})	0.291	1.165	0.282	1.047	0.998
Absorption correction	multi-scan	analytical	none	analytical	analytical
T_{min}	0.778	0.685		0.622	0.739
T_{max}	0.966	0.947		0.899	0.883
F(0 0 0)	220	1472	504	1600	856
Total data	6721	27744	12946	49514	13686
Unique data	2775	7029	3217	8632	4326
R_{int}	0.0281	0.0422	0.0576	0.0219	0.0157
R_σ	0.0206	0.0521	0.0528	0.0153	0.0128
Observed data [$I > 2\sigma(I)$]	2455	5283	2250	7862	4040
θ_{max} (°)	30.07	30.00	30.06	30.00	29.99
Ranges of h, k, l	−5, 8; −12, 12; −14, 14	−29, 29; −9, 10; −25, 25	−16, 16; −7, 8; −22, 22	−29, 29; −8, 9; −29, 29	−10, 10; −23, 23; −18, 17
Number of parameters	160	348	175	393	227
Flack's parameter x		0.48(3)			
R_1	0.0419	0.0371	0.0622	0.0322	0.0209
wR_2	0.1203	0.0700	0.1688	0.0741	0.0527
S	1.053	0.951	1.009	1.158	1.087
$\Delta\rho_{max}$ (e Å^{-3})	0.26	0.56	0.68	1.51	0.51
$\Delta\rho_{min}$ (e Å^{-3})	−0.38	−0.40	−0.38	−0.58	−0.63

factor were refined while the geometry was kept fixed. In the structures of the complexes, only H atoms refined isotropically were H atoms bound to the oxygen atoms in **2a**, and H atoms attached to C1 and to the heteroatoms in **2b**, while the other H atoms were refined using the riding model. The structure of **1a** was refined as twinned and consisted of two components with opposite polarities. The final BASF coefficient (Flack's parameter *x*) for **1a** was 0.48(3) [16,17]. Refinement was performed using SHELXL97 [18], geometry calculations were done using PLATON [19,20] and PARST [21,22], and the structure drawings were prepared using ORTEP [23].

2.3. NMR spectroscopy

All one- (^{1}H and APT), and gradient-selected two-dimensional (gCOSY, gHSQC and gHMBC) NMR spectra were recorded at ambient temperature on a Bruker Avance DRX500 and Bruker Avance DPX 300 spectrometers equipped with 5 mm inverse detection probe and dual probe, respectively. Sample concentration in DMSO-d_6 was 20 mg ml^{-1}. TMS was used as the internal standard.

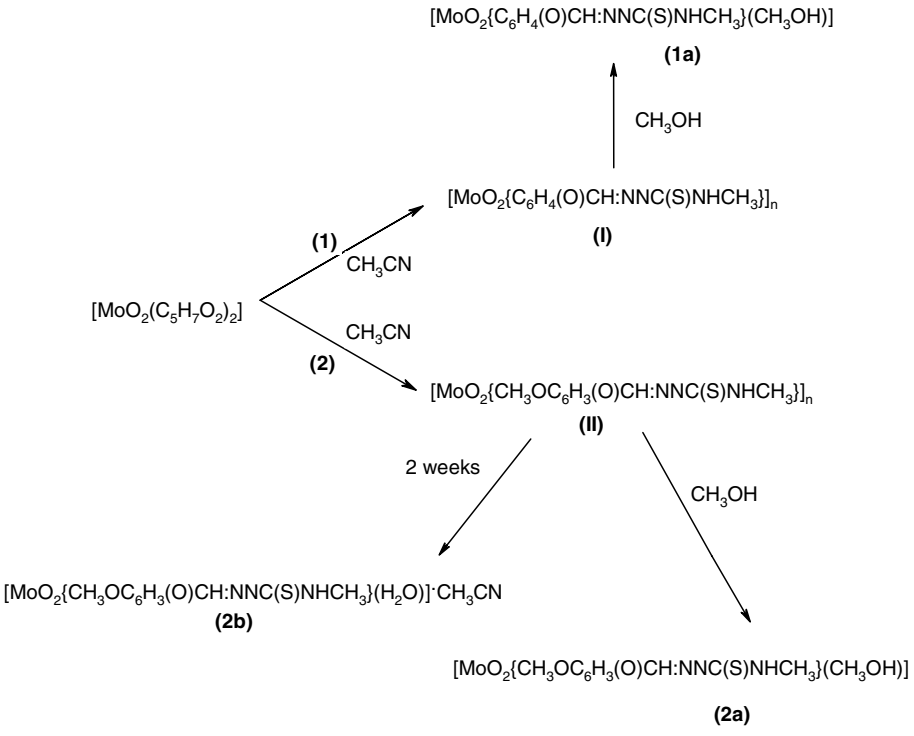
The typical spectral conditions for one-dimensional ^{1}H and ^{13}C (APT) spectra were as follows. The spectra were recorded using 64K data points and spectral widths of 7700 and 32 000 Hz for ^{1}H and ^{13}C experiments, respectively. Digital resolution was 0.12 and 0.48 Hz per point, respectively. The number of scans was 16 for ^{1}H and 500–1000 for APT spectra.

The COSY spectra were recorded under the following conditions: spectral width was 7700 Hz in both dimensions, 2K data points were applied in time domain and 512 increments were collected for each data set with linear prediction and zero filling to 2K. 8 scans were applied for each increment. Digital resolution was 6.50 Hz per point in both dimensions. The gradient selected inverse ^{1}H–^{13}C correlation experiments, gHSQC and gHMBC were recorded using the acquisition matrix of $1K \times 256$ with 16 and 32 scans, respectively, and processed with $2K \times 1K$ transformed matrix. The spectral width was 6600 Hz in f2 dimension and 32 000 Hz in f1 dimension for both experiments. Digital resolution was 3.25 Hz per point and 30.70 Hz per point in f2 and f1, respectively. HMBC spectra were recorded using a low-pass *J*-filter (3.4 s) and a delay for long-range coupling of 65 ms.

3. Results and discussion

3.1. Synthesis of the complexes

As a part of our studies [24–26] on molybdenum complexes with oxygen, sulfur and/or nitrogen donor



(1) $C_6H_4(OH)CH{:}NNC(SH)NHCH_3$ H_2SalTSC-4-Me

(2) $CH_3OC_6H_3(OH)CH{:}NNC(SH)NHCH_3$ H_2VanTSC-4-Me

Scheme 2.

ligands we describe here the syntheses and structures of molybdenum(VI) complexes coordinated by salicylaldehyde or by 3-methoxysalicylaldehyde 4-methylthiosemicarbazone ligand (Scheme 2). The brown polymeric complexes $[MoO_2\{SalTSC\text{-}4\text{-}Me\}]_n$ (**I**) and $[MoO_2\{VanTSC\text{-}4\text{-}Me\}]_n$ (**II**) were obtained by the reaction of $[MoO_2(C_5H_7O_2)_2]$ with a stoichiometric amount of corresponding thiosemicarbazone ligand in acetonitrile.

The monomeric complex $[MoO_2\{VanTSC\text{-}4\text{-}Me\}(H_2O)] \cdot CH_3CN$ (**2b**) was obtained when the filtrate of **II** was left at room temperature for two weeks. In **2b**, the molybdenum atom is additionally coordinated by a water molecule most probably from the atmospheric moisture and stabilized by the solvated acetonitrile molecule. Also, it should be mentioned that such a product was obtained only when the ligand was 3-methoxysalicylaldehyde 4-methylthiosemicarbazone. All attempts to isolate

Table 2
Selected bond distances (Å), angles (°) and torsion angles (°) for **1**, **1a**, **2**, **2a** and **2b**

Compound	**1**	**1a**		**2**	**2a**		**2b**
		A	**B**		**A**	**B**	
Bond distances							
O3–C6	1.3604(17)	1.336(5)	1.340(5)	1.363(3)	1.341(3)	1.342(3)	1.3418(17)
C6–11	1.3997(18)	1.410(6)	1.407(6)	1.395(3)	1.400(3)	1.407(3)	1.4035(19)
C11–C1	1.4501(18)	1.440(5)	1.453(5)	1.461(3)	1.449(3)	1.449(3)	1.4441(19)
C1–N1	1.2861(16)	1.298(5)	1.292(5)	1.287(3)	1.294(3)	1.292(3)	1.2999(18)
N1–N2	1.3763(16)	1.399(4)	1.419(4)	1.370(3)	1.409(2)	1.410(2)	1.3963(16)
N2–C3	1.3501(16)	1.319(6)	1.305(5)	1.363(3)	1.317(3)	1.317(3)	1.3137(18)
C3–S1	1.6833(13)	1.757(4)	1.766(4)	1.695(2)	1.763(2)	1.763(2)	1.7506(13)
C3–N4	1.3236(17)	1.332(5)	1.335(5)	1.326(3)	1.333(3)	1.335(3)	1.3430(17)
N4–C5	1.4484(18)	1.441(6)	1.442(6)	1.457(3)	1.453(3)	1.456(3)	1.4537(18)
Mo1–O1		1.686(3)	1.686(3)		1.7000(14)	1.7002(15)	1.6998(12)
Mo1–O2		1.706(3)	1.712(3)		1.7206(16)	1.7188(14)	1.7172(10)
Mo1–O3		1.927(3)	1.934(3)		1.9322(14)	1.9332(16)	1.9359(10)
Mo1–N1		2.265(3)	2.236(3)		2.2558(18)	2.2554(16)	2.2733(12)
Mo1–S1		2.4120(13)	2.4047(13)		2.4226(5)	2.4206(5)	2.4504(4)
Mo1–O4		2.399(3)	2.400(3)		2.3594(15)	2.3792(15)	2.3081(12)
Bond angles							
N1–C1–C11	122.60(11)	126.2(3)	124.8(3)	120.8(2)	125.0(2)	125.38(19)	126.79(12)
N2–N1–C1	114.94(11)	115.0(3)	113.8(3)	115.07(19)	113.88(17)	114.03(16)	112.95(11)
N1–N2–C3	121.89(11)	111.8(3)	111.4(3)	120.36(19)	112.34(17)	111.99(16)	114.24(11)
N2–C3–N4	117.46(12)	120.5(4)	121.3(4)	116.1(2)	120.5(2)	120.65(19)	118.86(12)
S1–C3–N2	118.54(10)	124.6(3)	124.3(3)	119.29(17)	124.18(16)	124.16(16)	125.37(10)
S1–C3–N4	124.00(10)	114.8(4)	114.4(3)	124.65(18)	115.29(16)	115.16(16)	115.78(10)
C3–N4–C5	123.87(12)	124.4(4)	124.1(4)	124.0(2)	123.22(19)	122.67(18)	122.85(12)
S1–Mo1–O1		96.54(11)	96.68(11)		96.26(6)	96.45(6)	96.19(4)
S1–Mo1–O2		90.33(12)	90.02(12)		91.05(5)	91.40(6)	91.33(4)
S1–Mo1–O3		153.37(9)	153.13(9)		153.82(5)	153.33(4)	154.71(3)
S1–Mo1–O4		83.54(8)	83.25(8)		84.16(4)	84.04(4)	81.38(3)
S1–Mo1–N1		74.71(8)	74.78(9)		74.90(5)	74.69(5)	75.84(3)
O1–Mo1–O2		105.43(16)	105.73(16)		104.92(7)	105.04(7)	105.27(5)
O1–Mo1–O3		98.95(13)	99.18(14)		97.99(7)	98.45(7)	98.66(5)
O1–Mo1–O4		172.34(13)	170.78(13)		172.31(7)	172.70(6)	169.91(4)
O1–Mo1–N1		95.51(13)	94.13(13)		94.79(7)	95.40(7)	92.66(5)
O2–Mo1–O3		106.12(14)	106.23(14)		106.24(7)	105.81(7)	104.25(4)
O2–Mo1–O4		82.23(14)	83.48(14)		82.74(6)	82.21(6)	84.62(5)
O2–Mo1–N1		155.60(14)	156.36(14)		157.02(7)	156.52(7)	159.08(5)
O3–Mo1–O4		78.27(11)	77.68(11)		78.87(6)	78.46(6)	80.43(4)
O3–Mo1–N1		82.32(11)	82.54(12)		82.11(6)	81.98(6)	83.11(4)
O4–Mo1–N1		77.09(10)	76.92(10)		77.88(7)	77.67(7)	77.25(4)
Torsion angles							
O3–C6–C11–C1	−2.53(19)	0.6(6)	2.3(6)	−1.2(3)	−0.4(3)	0.7(3)	1.5(2)
C6–C11–C1–N1	1.4(2)	−11.4(6)	−11.2(7)	−177.3(2)	12.7(3)	−12.9(3)	−5.2(2)
C11–C1–N1–N2	−176.74(11)	176.1(3)	173.8(4)	176.2(2)	−176.5(2)	176.6(2)	175.53(13)
C1–N1–N2–C3	175.50(12)	160.1(3)	158.3(4)	174.3(2)	−159.8(2)	158.0(2)	171.93(12)
N1–N2–C3–S1	−170.08(9)	−3.6(4)	−3.7(5)	175.18(16)	2.3(3)	−2.1(3)	4.69(18)
S1–C3–N4–C5	2.20(19)	−176.8(3)	−176.7(3)	1.7(3)	178.09(16)	−177.67(16)	−172.64(11)

In **1a** and **2a** two crystallographically independent complex molecules are labelled **A** and **B**.

the mononuclear molybdenum(VI) complex coordinated by a water molecule after isolation of complex **I** were unsuccessful even if some water was added to the solution. We believe that the electronic effect of the methoxy group attached to the phenolic ring 3-methoxysalicylaldehyde is responsible for the formation of this aqua complex.

We were also able to isolate monomeric orange crystals of $[MoO_2\{SalTSC\text{-}4\text{-}Me\}(CH_3OH)]$ (**1a**) and $[MoO_2\{VanTSC\text{-}4\text{-}Me\}(CH_3OH)]$ (**2a**) from the methanolic solution of **I** and **II**.

The IR data for thiosemicarbazone ligands are in accordance with the literature data [27]. The IR spectra of the complexes **I** and **II** showed characteristic strong vibrations at 806 and 808 cm^{-1}, respectively, assigned to the bridging Mo–O···Mo group which were absent in the case of mononuclear **1a**, **2a** and **2b** complexes. Also **I** and **II** showed single stretching frequencies at 920 and 923 cm^{-1}, respectively, assigned to ν(Mo=O), while the IR spectra of all three mononuclear complexes with the *cis*-MoO_2 core showed usual doublet at 933 and 891 cm^{-1} in **1a**, 934 and 889 cm^{-1} in **2a** and 932 and 892 cm^{-1} in **2b**.

The thermal analysis data of complexes **1a** and **2a** showed that their ligands decomposed in the range 224–554 °C and 222–512 °C, respectively, while those of complexes **1a**, **2a** and **2b** revealed two main processes:

(1) loss of coordinated methanol, water or acetonitrile within the range 92–141 °C in **1a**, 30–92 °C in **2a**; loss of coordinated water and acetonitrile in one step 30–95 °C in **2b**,
(2) complex decomposition occurring within the range 170–507 °C for **I**, 221–514 °C for **II** and 210–530 °C for **2b**.

3.2. Structural studies

Comparison of the selected bond distances, bond angles and torsion angles of the free ligands **1** and **2** and of their complexes **1a**, **2a** and **2b** is given in Table 2. Hydrogen bonding parameters are listed in Table 3.

3.2.1. Structures of ligands

Figs. 1 and 2 show ORTEP plots of the structures of the free ligand molecules **1** and **2**. Both molecules are found to be in the thioketo tautomeric form with the distances C3–S1 [1.6833(13) in **1** and 1.695(2) in **2**] and N2–C3 [1.3501(16) in **1** and 1.363(3) in **2**] similar to those found in the analogous thiosemicarbazone compounds [8,28–34]. The bond distances (Table 2) suggest electron delocalization throughout the thiosemicarbazone chain. The ligand molecules consist of two nearly planar moieties connected by a single N1–N2 bond: *N*-methylthioureide

Table 3
Hydrogen bonding geometry in structures **1**, **1a**, **2**, **2a** and **2b**

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(D–H···A) (°)
*Compound **1***				
N2–H2···O3^{i}	0.83(2)	2.50(3)	3.1285(18)	133(2)
O3–H3···N1	0.84(3)	1.92(3)	2.6846(17)	150(2)
N4–H4···N1	0.85(2)	2.33(2)	2.6961(16)	106.5(18)
*Compound **1a***				
N4A–H4A···O2B^{ii}	0.86	2.40	3.243(5)	166
N4B–H4B···O2A^{iii}	0.86	2.15	2.996(5)	169
O4A–H41A···N2B	0.93	1.93	2.819(4)	159
O4B–H41B···N2A^{iv}	0.93	2.01	2.911(4)	162
*Compound **2***				
N2–H2···O3^{v}	0.90(4)	2.13(3)	2.935(3)	148(3)
O3–H3···O5	0.82(4)	2.17(3)	2.631(3)	115(3)
O3–H3···S1^{v}	0.82(4)	2.50(4)	3.1861(19)	141(3)
N4–H4···N1	0.81(3)	2.31(3)	2.639(3)	105(3)
*Compound **2a***				
N4A–H4A···O2B	0.88	2.09	2.892(2)	151
N4B–H4B···O2A^{vi}	0.88	2.08	2.924(2)	160
O4A–H41A···N2A^{vii}	0.75(4)	2.10(4)	2.827(3)	165(3)
O4B–H41B···N2B^{viii}	0.76(3)	2.09(3)	2.851(2)	174(3)
*Compound **2b***				
N4–H4···O2^{ix}	0.80(2)	2.20(2)	2.9287(16)	151.2(18)
O4–H41···N2^{x}	0.81(3)	1.97(3)	2.7761(16)	173(3)
O4–H42···N3	0.80(3)	2.09(2)	2.8742(18)	168(2)

Symmetry codes: i = 1 + *x*, *y*, *z*; ii = 1−*x*, 1−*y*, −1/2 + *z*; iii = 3/2−*x*, 1/2 + *y*, 1/2 + *z*; iv = *x*, 1 + *y*, *z*; v = 2−*x*, 1−*y*, 1−*z*; vi = 1/2 + *x*, 3/2−*y*, 1/2 + *z*; vii = 1/2−*x*, −1/2 + *y*, 1/2−*z*; viii = 1/2−*x*, −1/2 + *y*, 3/2−*z*; ix = *x*, 3/2−*y*, −1/2 + *z*; x = 1−*x*, 1−*y*, −*z*.

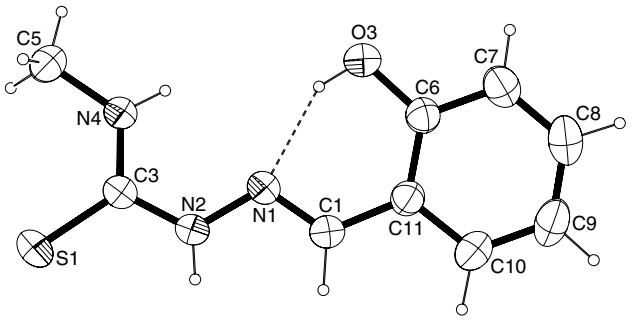


Fig. 1. ORTEP plot of the ligand molecule **1** with the atom labelling scheme. Ellipsoids are drawn at the 50% probability level. The O3–H3···N1 hydrogen bond is denoted by dashed line.

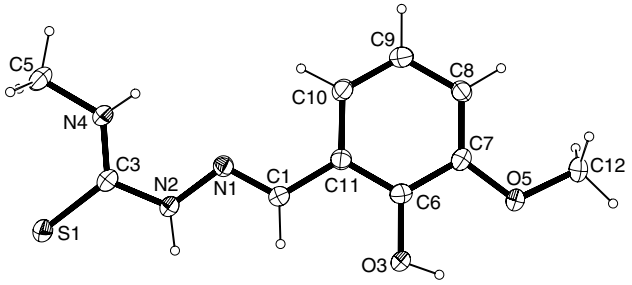


Fig. 2. ORTEP plot of the ligand molecule **2** with the atom labelling scheme. Ellipsoids are drawn at the 50% probability level.

fragment comprising N2, C3, S1, N4 and C5 [mean plane deviation of 0.007(6) Å in **1** and 0.0070(1) Å in **2**] and salicylaldimine fragment comprising N1, C1, C6–C11 and O3 [mean plane deviation of 0.0154(1) Å in **1** and 0.0160(1) Å in **2**]. Dihedral angles between these two planes are 12.54(3)° and 12.27(1)° for **1** and **2**, respectively. The atoms O5 and C12 from the methoxy group in **2**, although rather coplanar with others from the salicylaldimine fragment [mean plane deviation of 0.0237(1) Å], were excluded from the planarity calculations for the sake of comparability.

The striking difference between the molecular structures of the two ligands is the orientation of the phenyl ring moiety. In **1** the *syn* conformation of the C6 atom in respect to the N1 atom [torsion angle C6–C11–C1–N1 = 1.4(2)°] is stabilized by the intramolecular resonance-assisted O3–H3···N1 hydrogen bond, while in **2** the atoms C6 and N1 are *anti* to each other [torsion angle C6–C11–C1–N1 = –177.3(2)°] and O3–H3···O5 and O3–H3···S1 ($2-x$, $1-y$, $1-z$) hydrogen bonds are formed (Table 3). This seems to confirm an already given observation for the structures of the salicylaldehyde thiosemicarbazone derivates [31]: the intramolecular hydrogen bond between the hydroxyl group and the azomethine N atom would not be formed if another potential hydrogen bond acceptor for the hydroxyl H atom is present.

In the crystal structure of **1** molecules are interconnected by the N2–H2···O3 ($1+x$, y, z) hydrogen bonds thus forming chains parallel to the crystallographic *a* axis. In **2** a pair of molecules related by a centre of symmetry dimerize by forming the N2–H2···O3 ($2-x$, $1-y$, $1-z$) and O3–H3···S1 ($2-x$, $1-y$, $1-z$) hydrogen bonds. In both ligand structures there is an intramolecular hydrogen-bond-like contact N4–H4···N1.

3.2.2. Structures of complexes

Complex molecules found in the crystal structures of **1a** and **2a** are shown in Figs. 3 and 4, respectively. The asymmetric unit of structures **1a** and **2a** consists of two crystallographically independent complex molecules denoted as **A** and **B**. In **2b** the complex molecules cocrystallize with molecules of acetonitrile (Fig. 5).

The complex molecules consist of the *cis*-$[MoO_2]^{2+}$ core to which the doubly deprotonated tridentate ligand (**1** in **1a**; **2** in **2a** and **2b**) is meridionally bonded through the S1, N1 and O3 atoms. The sixth site of the distorted octahedral coordination around Mo is occupied either by methanol (in **1a** and **2a**) or water molecules (in **2b**).

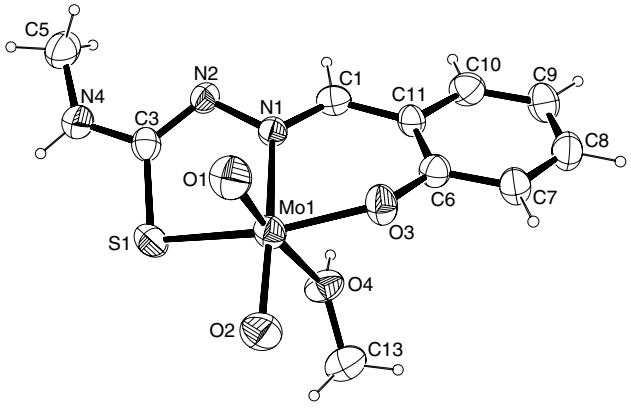


Fig. 3. ORTEP plot of the complex molecule **1aA** with the atom labelling scheme. Ellipsoids are drawn at the 50% probability level.

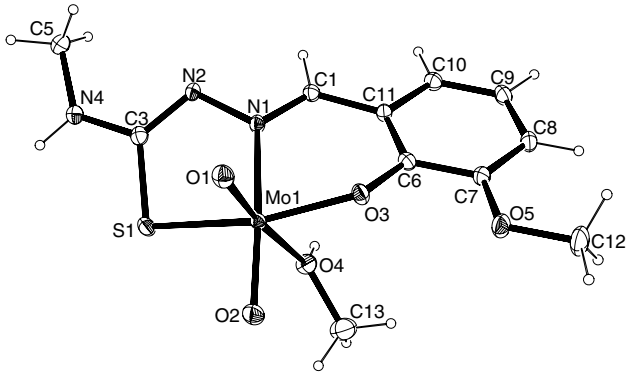


Fig. 4. ORTEP plot of the complex molecule **2aB** with the atom labelling scheme. Ellipsoids are drawn at the 50% probability level.

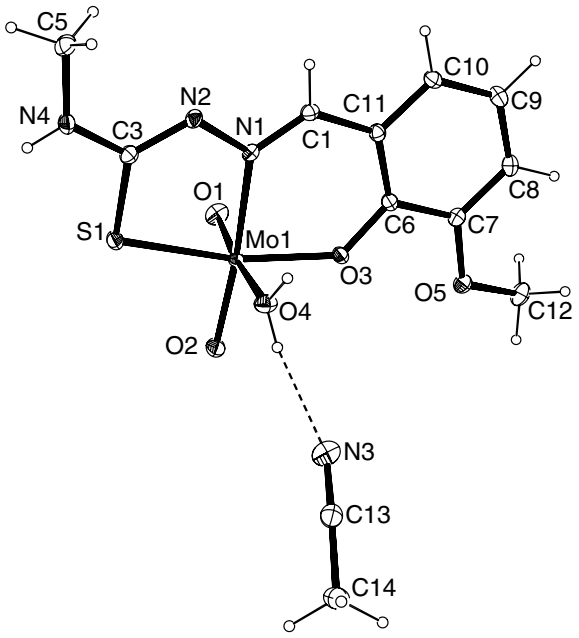


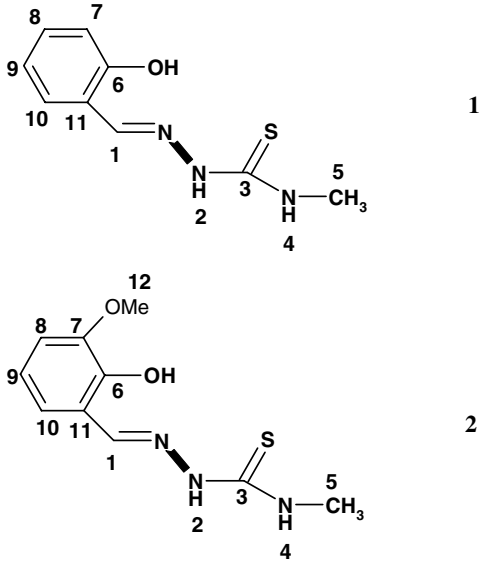
Fig. 5. ORTEP plot of the asymmetric unit of **2b** with the atom labelling scheme. Ellipsoids are drawn at the 50% probability level. The O4–H42···N3 hydrogen bond is represented by dashed line.

In all of the complex compounds, the Mo=O bond lengths [1.686(3)–1.7206(16) Å] and the O=Mo=O bond angles [104.92(7)–105.7(2)°] have values which are usual for *cis*-dioxomolybenum(VI) complexes. Also, the bond distances of Mo1–S1 [2.4047(13)–2.4504(4) Å], Mo1–N1 [2.236(3)–2.2733(12) Å] and Mo1–O3 [1.927(3)–1.9359(10) Å] are similar to those found in other thiosemicarbazonato molybdenum(VI) complexes [35–40]. The bond distances Mo1–O4 [2.359(2)–2.400(3) Å in **1a** and **2a**; 2.308(1) Å in **2b**] are significantly larger compared to the Mo1–O3.

As indicated by the bond distances N2–C3 [1.305(5)–1.319(6) Å] and C3–S1 [1.751(1)–1.766(4) Å], the ligands in the complexes are bonded in their enthiol form, i.e., in the tautomeric form different from that found in the structures of the free ligands (cf. in Table 2). In both bonded ligands, the C5 atom from the *N*-methyl group is *trans* relative to the S1 atom, while in the free ligands it is in the *cis* conformation. In order for ligands **1** and **2** to chelate the $[MoO_2]^{2+}$ moiety through the ONS donor set, as in the studied complexes, rotation of ~180° around the N2–C3 bond is necessary. Additionally for **2**, the phenyl ring moiety has to flip around the C11–C1 bond (Table 2). The 5- and 6-membered chelate rings thus formed (Mo1–N1–N2–C3–S1 and Mo1–O3–C6–C11–C1–N1) are not planar, but are rather puckered. In **1a** and **2a** the 5-membered chelate ring is close to the envelope conformation with Mo1 being the atom most out of the mean plane of the ring [ϕ_2 amounting to −3.5(2)° in the complex molecule **2aB** and 175.4(4)–176.8(2)° in **1a** and **2aA**], while the conformation of the 6-membered ring is nearly a screw-boat with the Mo1 and O3 atoms at the opposite sides of the mean plane of the ring [ϕ_2 amounting to −154.0(4)° in **2aB** and 24.1(4)–27.1(8)° in **1a** and **2aA**; θ amounting to −113.1(4)° in **2aB** and 65.8(8)–66.6(8)° in **1a** and **2aA**] [41,42]. The 5-membered chelate ring in **2b** is nearly planar [mean deviation of 0.0131(9) Å], but with conformation closer to twisted than to the envelope [ϕ_2 = 61(2)°] with C3 and S1 at the opposite sides of the mean plane. The 6-membered chelate ring conformation is almost an envelope with Mo1 being the atom most out of the mean plane of the ring [ϕ_2 = 7.7(3)° and θ = 59.2(3)°] [41,42].

Mean plane deviations for the *N*-methylthioureide [0.015(3) Å and 0.015(4) Å in **1a**; 0.010(2) and 0.012(2) Å in **2a**; 0.032(1) Å in **2b**] and the salicylaldimine [0.026(4) Å and 0.024(4) Å in **1a**; 0.034(2) Å and 0.030(2) Å in **2a**; 0.018(1) Å in **2b**] fragments (defined above for the structures of the ligands) show that in the molecules of the complexes these two fragments retain their planarity. But, in **1a** and **2a** dihedral angles between calculated RMS planes through the fragments [34.00(10)° and 36.64(9)° in **1a**; 35.05(4)° and 36.40(4)° in **2a**] are significantly different from those found in the free ligands. Also, torsion angles C1–N1–N2–C3 differ (Table 2), indicating rotation around the N1–N2 bond upon ligand binding. This is accompanied by the N1–N2 bond lengthening of ~0.02–0.04 Å. In **2b** the dihedral angle between the two fragments [10.74(4)°] and the C1–N1–N2–C3 torsion angle are both similar to those in **2**, but the N1–N2 bond lengthening of ~0.03 Å still occurs upon ligand binding.

In the crystal structure of **1a** two crystallographically independent molecules are bonded into dimers



Scheme 3.

Table 4
^{1}H and ^{13}C chemical shifts (ppm) of the ligands **1** and **2** and their molybdenum(VI) complexes **I** and **II**

Comp. atom	**1**		**I**		**2**		**II**	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1	8.37	139.09	8.57	152.10	8.39	138.93	8.54	152.37
2	11.47				11.43			
3		177.68				177.67		166.24
4	8.42		7.46		8.41		7.46	
5	3.01	30.96	2.81	31.32	3.00	30.95	2.80	31.62
6		156.46		159.09		146.01		149.19
7	6.87	116.16	6.82	118.44		148.06		149.43
8	7.22	131.09	7.41	133.74	6.96	112.83	7.10	116.21
9	6.83	119.32	6.98	121.26	6.78	119.03	6.92	121.37
10	7.95	126.72	7.60	133.95	7.55	118.17	7.18	125.48
11		120.62		121.61		121.05		122.19
12					3.81	56.02	3.77	56.59
OH	9.87				9.17			

by the O4A–H41A···N2B hydrogen bond. Such dimers are further connected in the infinite chain parallel to *b* axis by the O4B–H41B···N2A (x, $1 + y$, z) hydrogen bonds. Different chains are interlinked together by the hydrogen bonds formed between the amino N4–H4 and terminal oxygen O2 of the neighbouring molecule (Table 3).

Two molecules in the asymmetric unit of **2a** are connected by the N4A–H4A···O2B hydrogen bond. Similarly to **1a**, in the crystal structure of **2a**, there are also intermolecular hydrogen bonds between the amino N4–H4 and terminal oxygen O2 of the neighbouring molecule and between the methanol O4–H41 and the imine N2 from the symmetry equivalent molecule.

One hydrogen atom from the coordinated water molecule in the structure of **2b** participates in the hydrogen bonding with the cocrystallized acetonitrile molecule (Fig. 5), while the other hydrogen atom is part of the hydrogen bond with the imine N2 atom from the molecule related by an inversion centre. The centrosymmetrical dimers formed in this way are further connected by the intermolecular hydrogen bonds between the amino N4–H4 and the terminal oxygen O2 (also observed in **1a** and **2a**).

3.3. NMR spectroscopy

The complete ^{1}H and ^{13}C atom assignments in DMSO-d_6 were made on the basis of the combined use of several one- (^{1}H and APT sequences) and two-dimensional homo- and heteronuclear experiments (COSY, HSQC and HMBC sequences). The proton and carbon chemical shifts of the ligands **1** and **2** (Scheme 3) and complexes **1a** and **2a** are given in Table 4.

The observed chemical shift values are similar to those reported previously for the related thiosemicarbazone ligands and their molybdenum(VI) complexes [40]. In the proton NMR spectra of the free ligands a broad OH signal was observed at 9–10 ppm indicating a participation of this hydroxyl proton in an intramolecular O–H···N1 hydrogen bonds in DMSO, which is in line with our previous results. Carbon chemical shifts and HMBC correlation peaks have confirmed that both ligands exist in the thioketo form in solution, as also found in the solid state. The absence of OH and N2H protons in the proton spectra of **1a** and **2a** corroborates a formation of the complexes with molybdenum. An up-field shift of N4H protons of about 1 ppm (Table 4) is in accordance with this. Slight coordination induced down-field shifts have also been observed for H1 protons. The largest changes in carbon chemical shifts in **1a** and **2a** have been found for carbons at the two interacting sites, C-1 and C-3. The down-field shifts of up to 13.4 ppm for the former and up-field shifts of approximately 11.0 ppm for the latter were observed. The shielding effects at C-3 arised from two contributions, i.e. from a coordination induced-shift and from the formation of an imine C=N bond in the complex instead of a thiocarbonyl C=S bond in the ligand. The carbon atoms at the third interacting site, e.g., C-6 exhibited only moderate chemical shift changes, as already found for the related molybdenum complexes with thiosemicarbazone donors.

4. Supplementary material

CCDC nos. 260969, 260970, 260971, 260972 and 260973 contain the supplementary crystallographic data for compounds **1**, **1a**, **2**, **2a** and **2b**, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336033.

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