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Synthesis and structure of lipophilic dioxo-molybdenum (VI) bis(hydroxamato) complexes

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ABSTRACT

New methods for the synthesis of complexes of molybdenyl with hydrophobic alkyl-substituted hydroxamic acids have been developed. A number of novel coordination compounds of the general formula MoO_2L_2 (where HL is decano-, N-methyl-decano-, N-methyl-hexano-, N-methyl-1-adamantano- and N-*tert*-butyl-hexanohydroxamic acids) have been synthesized. All compounds obtained have been characterized by IR, ^1H NMR spectroscopy and X-ray crystallography. The effect of the electron donating and steric properties of ligand substituents on the structure of complexes is discussed.

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1. Introduction

The richness of the coordination chemistry of hydroxamic acids stimulates extensive scientific researches in different areas of technology. As an example, it has been found recently that oxo- and oxoperoxo-molybdenum (VI) hydroxamato complexes possess unique properties (selectivity and high desired-product yield) of catalysts for the oxidation of olefins to epoxides [1]. However, the overwhelming majority of publications dealing with metal and metalloid hydroxamato complexes relate to chemical biology and medicinal chemistry, which is reflected in an excellent review article by Codd [2].

It is widely accepted that lipophilic compounds have a better cellular permeability than hydrophilic ones. A number of complexes of vanadyl and vanadate with hydroxamic acids as suitable hydrophobic ligands showed a considerable glucose-lowering activity in tests on experimental diabetic mice [3]. For a number of potentially anti-diabetic and at the same time hydrophobic complexes of the general formula MoO_2L_2, where HL is 2,4-pentanedione, L-cysteine ethyl ester, N,N-diethyldithiocarbamic acid, a ligand-exchange mechanism of assimilation of $[MoO_4]^{2-}$ anion by biological media, including erythrocytes, has been established [4]. The presence of aliphatic substituents in hydroxamic acids gives high lipophilicity to them as proligands and to their coordination compounds [5]. A number of N-methyl substituted hydroxamic acids have been patented as active substances of drugs [6].

The present article describes methods, developed by us, for the synthesis of complexes of molybdenyl with hydroxamic acids containing aliphatic substituents both at the nitrogen atom and at the carbonyl carbons. The following novel coordination compounds have been synthesized and investigated: bis(decanohydroxamato)-dioxo-molybdenum, (VI) $MoO_2(DH)_2$ (**1**); bis(N-methyl-decanohydroxamato)-dioxo-molybdenum (VI), $MoO_2(N\text{-}MDH)_2$ (**2**); bis- (N-methyl-hexanohydroxamato)-dioxo-molybdenum (VI), $MoO_2(N\text{-}MHH)_2$ (**3**); bis(N-*tert*-butyl-hexanohydroxamato)-dioxo-molybdenum (VI), $MoO_2(N\text{-}tBuHH)_2$ (**4**); bis(N-methyl-1-adamantanohydroxamato)-dioxo-molybdenum (VI), $MoO_2(N\text{-}MAdH)_2$ (**5**) (Scheme 1).

2. Experimental

2.1. Materials

2,4-Pentanedione, *tert*-butylamine, triethylamine, benzoyl peroxide, benzene, toluene, methanol of Merck; 1-adamantanecarbonyl chloride, hexanoyl chloride, decanoyl chloride, N-methyl-hydroxylamine hydrochloride, hydroxylamine hydrochloride, ethyl decanoate, molybdenum trioxide of Aldrich; dimethylacetamide of Lab-Scan were used as original substances and solvents without additional purification. Dimethylformamide (DMF) of Merck was purified as was described by us earlier [7]. All chemicals used were of reagent grade. Silica gel TLC plates of Merck were used for qualitative analysis. Bis(2,4-pentanedionato)-dioxo-molybdenum (VI), $MoO_2(acac)_2$, has been synthesized by a known procedure [8].

Molybdenum dioxodichloride, MoO_2Cl_2, was prepared by substantially modifying a published method [9]. The stock, which

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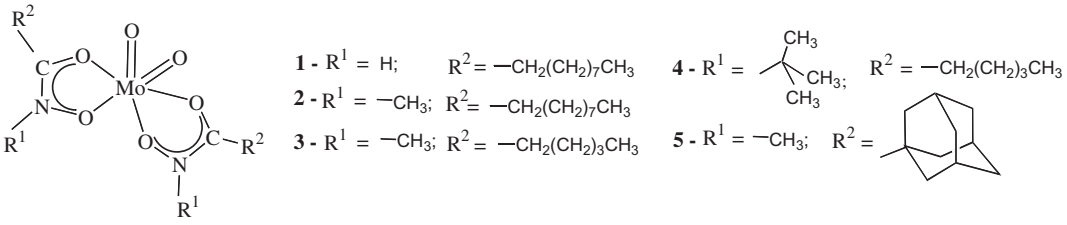


Scheme 1.

was prepared by grinding 29.0 g (0.201 mol) of molybdenum trioxide and 11.8 g (0.201 mol) of sodium chloride in a porcelain mortar, was placed in a tubular quartz reactor with a gas inlet on the one side and a device for receiving the sublimed product on the other side. This device consists of a coaxial two-necked round-bottom flask, a glass rod with a Teflon scraper and a rod guide equipped with gas outlet. On gradual heating (~5 °C/min) with a tube furnace in an argon stream (~10 l/h) above 400 °C, molybdenum dioxodichloride sublimate appears on the cold part of the reactor, which is removed with the scraper into the receiving flask. After the reaction mixture has reached a temperature of ~600 °C, sublimate condensation continues for another *ca.* 1 h. Without interrupting argon supply, the receiving flask with yellowish-white crystalline product is detached sequentially from the rod guide and tubular reactor and is then quickly sealed with stoppers; the compound obtained is transferred in a dry box to a storage bottle. MoO_2Cl_2 yield: 5.9 g (~30% in terms of MoO_3).

2.2. Synthesis of the proligands

Decanohydroxamic acid (DHA) has been synthesized by the procedure presented in [10], m.p. 88–89 °C (lit. 88 °C [11]). IR (KBr, cm^{-1}): 3260, 3060, 2945, 2920, 2840, 2760, 1665, 1623, 1565, 1467, 1420, 1113, 1080, 1055, 1050, 1045, 1012, 985, 968, 740, 721, 650, 559, 495, 480, 445. ^1H NMR (300 MHz, DMSO-d_6, 25 °C, TMS), δ, ppm: 10.31 (s, 1H, NH), 8.64 (s, 1H, OH), 1.92 (m, 2H, β-CH_2), 1.47 (m, 2H, γ-CH_2), 1.24 (m, 12H, $(CH_2)_6$), 0.86 (t, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3).

N-methyl-hexanohydroxamic acid (N-MHHA) and N-methyl-decanohydroxamic acid (N-MDHA) have been synthesized by a procedure analogous to that for N-methyl-acetohydroxamic acid [12].

N-MHHA: To a mixture of sodium carbonate (0.1 mol, 10.6 g) and N-methyl-hydroxylamine hydrochloride (0.1 mol, 8.35 g) in 160 ml of dry methanol was added dropwise hexanoyl chloride (0.1 mol, 13.5 g) with stirring at a temperature of not over 5 °C (cooling ice bath). After the termination of addition, the reaction mixture was stirred for another 0.5 h and then filtered; the solvent was removed on a rotary evaporator. The residue was filtered again and distilled *in vacuo, b.p. 70–72* °C, 12 Pa (lit. [6] 87–90 °C; 0.1 mm Hg). Yield: 7.5 g, 52%. *Anal.* Calc. for $C_7H_{15}NO_2$ (MW 145.21): C, 57.90; H, 10.41; N, 9.65. Found: C, 58.11; H, 10.32; N, 9.34%. IR (film, cm^{-1}): 3191, 2960, 2941, 2871, 1630, 1615, 1510, 1470, 1445, 1397, 1206, 1100, 943, 900, 843, 721, 615, 503. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS), δ, ppm: 8.61 (br.s, 1H, OH), 3.33 (s, 3H, N-CH_3), 2.42 (m, 2H, β-CH_2), 1.63 (m, 2H, γ-CH_2), 1.32 (m, 4H, $(CH_2)_2$), 0.90 (t, $^3J_{H-H}$ = 6.8 Hz, 3H, CH_3).

N-MDHA was prepared in much the same way, taking decanoyl chloride (0.1 mol, 19.1 g) as a basis. Yield: 10.3 g, 51%, b.p. 132–135 °C, 12 Pa, m.p. 36–37 °C. *Anal.* Calc. for $C_{11}H_{23}NO_2$ (MW 201.32): C, 65.63; H, 11.52; N, 6.96. Found: C, 65.48; H, 11.43; N, 7.02%. IR (KBr, cm^{-1}): 3141, 2956, 2919, 2860, 1636, 1601, 1492, 1466, 1445, 1408, 1390, 1191, 1130, 1105, 1066, 1056, 962, 935, 873, 808, 761, 729, 706, 673, 618, 558, 530, 458, 423, 412, 402. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS), δ, ppm: 8.52 (br.s, 1H, OH), 3.35 (s, 3H, N-CH_3), 2.32 (m, 2H, β-CH_2), 1.65 (m, 2H, γ-CH_2), 1.23 (m, 12H, $(CH_2)_6$), 0.88 (t, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3).

N-methyl-1-adamantanohydroxamic acid (N-MAdHA) was synthesized by the somewhat changed above procedure, namely, 1-adamantanocarbonyl chloride (0.1 mol, 19.9 g) was added dropwise to the reaction mixture as a solution in dry ether; the product obtained was purified by sublimation (bath temperature 65 °C, 12 Pa). Yield: 9.4 g, 45%., m.p. 111–112 °C (lit. [13] 112–113 °C). *Anal.* Calc. for $C_{12}H_{19}NO_2$ (MW 209.29): C, 68.87; H, 9.15; N, 6.69. Found: C, 68.67; H, 9.25; N, 6.73%. IR (KBr, cm^{-1}): 3152, 2915, 2850, 1594, 1587, 1514, 1455, 1419, 1393, 1360, 1321, 1263, 1209, 1182, 1107, 1071, 986, 957, 911, 798, 727, 694, 526, 465. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS); δ, ppm: 8.54 (br.s, 1H, OH), 3.46 (s, 3H, N-CH_3), 2.05 (m, 3H, γ-CH of Ad), 2.01 (m, 6H, β-CH_2 of Ad), 1.73 (m, 6H, δ-CH_2 of Ad).

2.3. Synthesis of the complexes

2.3.1. Method 1

To a solution of proligand (30 mmol) and triethylamine (30 mmol, 3.03 g) in dry DMF (100 ml) was added dropwise a solution of molybdenum (VI) dioxydichloride (15 mmol, 2.98 g) in dry DMF with vigorous stirring in argon atmosphere. After the termination of addition, the lemon yellow colour reaction mixture was stirred for another 3 h. The starting substances were fed and the reaction was carried out in complete isolation from atmospheric moisture. After the termination of stirring, the $(C_2H_5)_3N{\cdot}HCl$ precipitate formed was filtered off and washed on a filter with three 3 ml portions of DMF; the solvent was evaporated under 25 hPa vacuum. The solid yellow precipitate was dried under 12 Pa vacuum at 50 °C to remove the traces of the solvent; pure complexes were isolated by crystallization.

2.3.2. Method 2 (ligand-exchange route)

The synthesis was carried out by gradual and continuous distilling of acetylacetone at 13 hPa and 60 °C off a solution of bis-(2,4-pentanedionato)-dioxo-molybdenum (VI) (5 mmol, 1.63 g) in 150 ml of dimethylacetamide containing appropriate hydroxamic acid (10 mmol). The course of the process was monitored and its exchange mechanism verified by means of a qualitative reaction of $FeCl_3$ with acetylacetone contained in the distillate. After the process was complete, the solid residue was held under 12 Pa vacuum at 50 °C for 2 h to remove the traces of the solvent; pure complexes were isolated by crystallization.

2.3.3. Method 3

Molybdenum trioxide (15 mmol, 2.16 g) was dissolved under vigorous stirring in 100 ml of distilled water, adding dropwise a 50% solution of sodium hydroxide up to pH 12. The volume of the solution was brought to 150 ml by adding water. While stirring was continued a solution of 30 mmol proligand in 150 ml of ethanol was added to the aqueous solution obtained. To the yellowish reaction mixture was added dropwise a 6 N HCl solution up to pH

3. After 3 h of stirring the reaction mixture, the intensity of its lemon yellow colour increased greatly, and a suspended solid phase appeared. After holding the reaction mixture at 5 °C for 8 h, the abundant light yellow precipitate was filtered off, washed on a filter with three 10 ml portions of cooled ethanol–water mixture, taken in a 1/1 ratio, and dried under 12 Pa vacuum at 50 °C to remove the traces of the solvent. Pure complexes were isolated by recrystallization.

2.3.4. Bis(decanohydroxamato)-dioxo-molybdenum (VI)

Complex **1** was prepared by the method 1, taking decanohydroxamic acid (30 mmol, 5.62 g) as a basis, and purified by crystallization from an ethanol–water mixture (2/1) at 5 °C. Yield: 7.21 g, 96%. *Anal.* Calc. for $C_{20}H_{40}N_2O_6Mo$ (MW 500.49): C, 48.00; H, 8.06; N, 5.60. Found: C, 49.12; H, 7.91; N, 5.75%. M.p. 159–160 °C, decomp. 177–180 °C. IR (KBr, cm^{-1}): 3160, 3025, 2945, 2920, 2843, 1565, 1515, 1456, 1424, 1365, 1355, 1295, 1115, 1062, 1002, 988, 945, 925, 890, 765, 725, 702, 608, 555, 545, 485. ^1H NMR (300 MHz, DMSO-d_6, 25 °C, TMS), δ, ppm: 13.23 (s, 1H, NH), 2.26 (m, 2H, β-CH_2), 1.49 (m, 2H, γ-CH_2), 1.23 (m, 12H, $(CH_2)_6$), 0.86 (t, $^3J_{H-H}$ = 7.0 Hz, 3H, CH_3).

Complex **1** was also prepared by the method 2, taking decanohydroxamic acid (10 mmol, 1.87 g) as a basis, and purified by crystallization from an ethanol–water mixture (2/1) at 5 °C. Yield: 2.1 g, 84%. The compound was identified by its melting point and by comparing IR spectra of samples prepared by the methods 1 and 2.

2.3.5. Bis(N-methyl-decanohydroxamato)-dioxo-molybdenum (VI)

Complex **2** was prepared by the method 1, taking N-methyl-decanohydroxamic acid (30 mmol, 6.04 g) as a basis, and purified by crystallization from ethanol at −10 °C. Yield: 7.45 g, 94%. *Anal.* Calc. for $C_{22}H_{44}N_2O_6Mo$ (MW 528.54): C, 49.99; H, 8.39; N, 5.30. Found: C, 49.86; H, 8.25; N, 5.43%. M.p. 71–72 °C, decomp. 195–198 °C. IR (KBr, cm^{-1}): 2928, 2848, 1580, 1492, 1471, 1422, 1234, 1156, 1119, 1070, 1014, 993, 963, 922, 884, 812, 790, 756, 729, 710, 673, 651, 605, 582, 524, 504, 458. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS), δ, ppm: 3.51 (s, 3H, N-CH_3), 2.42 (m, 2H, β-CH_2), 1.67 (m, 2H, γ-CH_2), 1.26 (m, 12H, $(CH_2)_6$), 0.88 (t, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3).

Complex **2** was also prepared by the method 3, taking N-methyl-decanohydroxamic acid (30 mmol, 6.04 g) as a basis, and purified by crystallization from ethanol at −10 °C. Yield: 7.2 g, 91%. The compound was identified by its melting point and by comparing IR spectra of samples prepared by the methods 1 and 3.

2.3.6. Bis(N-methyl-hexanohydroxamato)-dioxo-molybdenum (VI)

Complex **3** was prepared by the method 2, taking N-methyl-hexanohydroxamic acid (10 mmol, 1.45 g) as a basis, and purified by crystallization from toluene at 5 °C. Yield: 1.56 g, 75%. *Anal.* Calc. for $C_{14}H_{28}N_2O_6Mo$ (MW 416.32): C, 40.39; H, 6.78; N, 6.73. Found: C, 40.24; H, 6.86; N, 6.61%. M.p. 85–87 °C, decomp. 197–199 °C. IR (KBr, cm^{-1}): 2960, 2938, 2865, 1583, 1484, 1422, 1383, 1338, 1280, 1232, 1212, 1156, 1112, 1000, 956, 918, 882, 800, 748, 734, 687, 675, 651, 605, 580, 522, 502, 463, 441, 410. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS), δ, ppm: 3.51 (s, 3H, N-CH_3), 2.40 (m, 2H, β-CH_2), 1.67 (m, 2H, γ- CH_2), 1.32 (m, 4H, $(CH_2)_2$), 0.90 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3).

Complex **3** was also prepared by the method 3, taking N-methyl-hexanohydroxamic acid (30 mmol, 4.36 g) as a basis, and purified by crystallization from toluene at 5 °C. Yield: 5.56 g, 89%. The compound was identified by its melting point and by comparing IR spectra of samples prepared by the methods 2 and 3.

2.3.7. Bis(N-tert-butyl-hexanohydroxamato)-dioxo-molybdenum (VI)

Complex **4** was prepared without intermediate isolation of proligand, N-*tert*-butyl-hexanohydroxamic acid. A mixture of hexanoyl chloride (100 mmol, 13.36 g), O-benzoyl-N-*tert*-butylhydroxylamine (100 mmol, 19.33 g) [14] and pyridine (100 mmol, 7.91 g) in 100 ml of dry benzene was stirred at 70 °C for 6 h. Then the reaction mixture was sequentially washed with dilute HCl, a saturated solution of $NaHCO_3$ and water and dried over Na_2SO_4. Benzene was evaporated *in vacuo,* and raw N-hexanoyl-O-benzoyl-N-*tert*-butylhydroxylamine was obtained. To a solution of the above product in methanol (200 ml) was added a solution of NaOH (200 mmol, 8.0 g) in 40 ml of water, and the mixture was stirred vigorously for 2 h; then a solution of 30 mmol (7.26 g) of sodium molybdate dihydrate in 150 ml of water was added to the reaction mixture, and the pH value was adjusted to 12.0. To the almost homogeneous yellowish solution was added dropwise a 6 N HCl solution up to pH 3.0. After subsequent 3 h of stirring the reaction mixture, the yellowish emulsion obtained was diluted twofold with water and extracted with three 50 ml portions of chloroform. Combined chloroform extracts were washed with water and dried over Na_2SO_4. The solvent was evaporated on a rotary evaporator, and the semisolid dark-yellow residue was held for 8 h under 12 Pa vacuum at 50 °C to completely remove the volatile organic impurities. The complex was purified by thrice-repeated crystallization from an ethanol–water (1/1) mixture at 5 °C. Yield: 7.23 g. *Anal.* Calc. for $C_{20}H_{40}N_2O_6Mo$ (MW 500.49): C, 48.00; H, 8.06; N, 5.60. Found: C, 49.18; H, 7.95; N, 5.43%. M.p. 63–65 °C, decomp. 186–191 °C. IR (KBr, cm^{-1}): 2963, 2928, 2864, 1529, 1466, 1405, 1371, 1312, 1282, 1254, 1234, 1214, 1123, 1113, 1055, 1033, 1022, 978, 952, 916, 883, 808, 755, 718, 651, 623, 572, 542, 490, 435. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS), δ, ppm: 2.56 (m, 2H, β-CH_2), 1.67 (m, 2H, γ-CH_2), 1.57 (s, 9H, $C(CH_3)_3$), 1.32 (m, 4H, $(CH_2)_2$), 0.90 (t, $^3J_{H-H}$ = 7.0 Hz, 3H, CH_3).

2.3.8. Bis(N-methyl-1-adamantanohydroxamato)-dioxo-molybdenum (VI)

Complex **5** was prepared by the method 1, taking N-methyl-1-adamantanohydroxamic acid (30 mmol, 6.28 g) as a basis, and purified by crystallization from ethanol. Yield: 7.52 g, 92%. *Anal.* Calc. for $C_{24}H_{36}N_2O_6Mo$ (MW 544.49): C, 52.94; H, 6.66; N, 5.14. Found: C, 53.12; H, 6.81; N, 5.08%. Mp (decomp.) 207–208 °C. IR (KBr, cm^{-1}): 2907, 2850, 1548, 1458, 1405, 1374, 1352, 1320, 1271, 1227, 1193, 1161, 1111, 1068, 998, 970, 942, 916, 894, 831, 799, 759, 702, 656, 635, 599, 540, 466. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS), δ, ppm: 3.68 (s, 3H, N-CH_3), 2.08 (m, 3H, γ-CH of Ad), 1.99 (m, 6H, β-CH_2 of Ad), 1.73 (m, 6H, δ-CH_2 of Ad).

Complex **5** was also prepared by the method 3, taking N-methyl-1-adamantanohydroxamic acid (30 mmol, 6.28 g) as a basis; and purified by crystallization from ethanol. Yield: 7.03 g, 86%. The compound was identified by its melting point and by comparing IR spectra of samples prepared by the methods 1 and 3.

2.4. Physical measurements

The IR spectra were recorded in KBr pellets in a range of 4000–400 cm^{-1} on a Specord M80 spectrophotometer equipped with an IBM-compatible operating computing system. The elemental analysis has been carried out on a Carlo Erba 1106 analyzer. The ^1H NMR spectra were recorded on a Varian VXR-300 spectrometer in $CDCl_3$ and DMSO-d_6 solutions with an internal TMS standard.

2.5. X-ray crystallography

The structure of compounds **1–5** was determined by X-ray crystallography. The reflection intensity measurements were performed on a single crystal diffractometer Bruker Smart Apex2

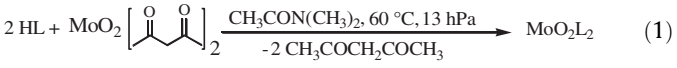
with Mo Kα radiation (λ = 0.71073 Å), graphite monochromator at 100 K using ω- and φ-scan techniques. The unit cell parameters of the compounds **1–4** were determined from 3 short ω-scans from different crystal orientations using RLATT program from SHELXTL package [15]. Reflection intensities were integrated using SAINT software [16] and corrected for Lorentz effect, polarization and absorption by a numerical (1–3) and a semi-empirical (4) technique using SADABS [17]. In the case of **5**, the CELL_NOW program [15] was used for the determination of cell parameters and independent domain orientations. As a result, 4 independent orientation matrixes were found, which indicates nonmerohedral twinning in the crystal. The intensity data of **5** was integrated using four orientation matrixes at the same time. TWINABS program [18] was used for semi-empirical absorption correction of the intensity data and produced HKLF4 (for solving structure) and HKLF5 (for anisotropic refinement) files. The structures **1–4** were solved by direct methods and refined anisotropically for all non-hydrogen atoms by full matrix least squares on F^2 using SHELXTL program package [15]. All hydrogen atoms bonded to carbon atoms are positioned geometrically to idealized positions and refined using riding model with constrained isotropic parameters: $U_{iso}(H) = 1.2U_{iso}(C)$ for CH_2 and $U_{iso}(H) = 1.5U_{iso}(C)$ for CH_3. The single crystal of **1** poorly scattered at higher angles ($2\theta > 40°$), which causes an effect on R_{int} value and, as a result, on precision parameters of the model. During the structure refinement of **3**, half of disordered toluene molecule was found in the crystal structure near the crystallographic inversion centre. The use of distance constraints did not give a significant effect. Therefore, the SQUEEZE routine in PLATON [19] was used to modify the reflection data for obtaining a reasonable model without solvent molecule. The molar ratio of complex **3** is one toluene molecule per two molecules of complex. The presence of toluene molecule in the structure is taken into consideration in experimental data table (empirical formula, molecular weight, calculated density, $F(0\,0\,0)$). The main experimental data is given in Table 1.

3. Results and discussion

3.1. Synthesis and spectroscopy

Dioxomolybdenum (VI) coordination compounds can be prepared by various methods, depending on which of the precursors: Na_2MoO_4, MoO_2Cl_2 or $MoO_2(acac)_2$ is used as the source of the central atom of these complexes [20].

The use of $MoO_2(acac)_2$ as a precursor in syntheses of complexes with tetradentate [21] and tridentate [22] proligands seems to us to offer no problems since the ligand-exchange reaction in these cases is promoted by an entropy effect. At the same time, the use of the above precursor in syntheses with potentially bidentate proligands calls for special conditions for carrying out the reaction since 2,4-pentanedione in itself is a bidentate proligand, and there is therefore a certain probability of formation of mixed-ligand complexes [20]. Both the starting compounds and complexes of hydroxamic acids with molybdenyl are practically nonvolatile under low vacuum conditions. Therefore, the removal of acetylacetone by distilling it off continuously together with dimethylacetamide allows one to effectively shift the equilibrium ligand-exchange process towards the formation of desired products with acceptable yield.



(1)

Table 1
Crystal data and structure refinement for compounds **1–5**.

Compound No.	1	2	3	4	5
Empirical formula	$C_{20}H_{40}MoN_2O_6$	$C_{22}H_{44}MoN_2O_6$	$C_{14}H_{28}MoN_2O_6{\cdot}0.5C_7H_8$	$C_{20}H_{40}MoN_2O_6$	$C_{24}H_{36}MoN_2O_6$
Formula weight	500.48	528.53	461.89	500.48	544.49
Crystal system, space group	Orthorhombic, *Pbca*	Triclinic, $P\bar{1}$	Monoclinic, C_2/c	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Unit cell dimensions					
a (Å)	17.396(3)	7.8689(2)	26.0611(10)	9.2630(2)	13.815(7)
b (Å)	8.9742(16)	11.0538(2)	7.9568(3)	10.8550(2)	13.862(3)
c (Å)	30.906(5)	15.597(1)	22.6052(9)	13.5810(3)	14.224(3)
α (°)		100.973(1)		68.063 (1)	91.08(3)
β (°)		98.442(1)	114.499(2)	77.804(1)	104.26(4)
γ (°)		94.055(1)		73.530(1)	116.43(2)
Volume (Å^3)	4825.1(14)	1310.60(9)	4265.5(3)	1206.17(4)	2338.0(14)
Z	8	2	8	2	4
D_{calc} (g/cm^3)	1.378	1.339	1.438	1.378	1.547
μ (mm^{-1})	0.579	0.536	0.648	0.579	0.604
$F(0\,0\,0)$	2112	560	1924	528	1136
Crystal size (mm)	0.33 × 0.11 × 0.04	0.47 × 0.29 × 0.04	0.50 × 0.33 × 0.14	0.29 × 0.13 × 0.08	0.40 × 0.35 × 0.04
θ Range (°)	1.76–25.00	2.08–26.40	1.72–26.40	1.63–26.40	1.49–26.50
Limiting indices					
	$-17 \leqslant h \leqslant 20$	$-9 \leqslant h \leqslant 9$	$-32 \leqslant h \leqslant 32$	$-11 \leqslant h \leqslant 11$	$-17 \leqslant h \leqslant 16$
	$-10 \leqslant k \leqslant 10$	$-13 \leqslant k \leqslant 13$	$-9 \leqslant k \leqslant 9$	$-13 \leqslant k \leqslant 13$	$-17 \leqslant k \leqslant 17$
	$-36 \leqslant l \leqslant 21$	$-19 \leqslant l \leqslant 19$	$-28 \leqslant l \leqslant 28$	$-16 \leqslant l \leqslant 16$	$0 \leqslant l \leqslant 17$
Reflections collected/unique	20814/4238	26724/5371	19972/4365	12900/4920	13649/13649
	R_{int} = 0.1216	R_{int} = 0.0994	R_{int} = 0.0290	R_{int} = 0.0222	R_{int} = 0.0000
Completeness to θ_{max}	99.6	99.8	99.9	99.3	89.6
Absorption correction	Numerical	Numerical	Numerical	Semi-empirical	Semi-empirical
Maximum/minimum transmission	0.9761/0.8320	0.9789/0.7866	0.9169/0.7415	0.9573/0.8492	0.9751/0.7932
Data/restraints/parameters	4238/2/270	5371/0/284	4365/0/212	4920/0/270	13649/0/603
Goodness-of-fit (GOF) on F^2	1.058	0.967	1.102	1.031	1.063
Final *R* indices[a] [$I > 2\sigma(I)$]	R_1 = 0.0743	R_1 = 0.0379	R_1 = 0.0312	R_1 = 0.0226	R_1 = 0.0578
	wR_2 = 0.1675	wR_2 = 0.0719	wR_2 = 0.0749	wR_2 = 0.0519	wR_2 = 0.1376
R indices[a] (all data)	R_1 = 0.1145	R_1 = 0.0551	R_1 = 0.0333	R_1 = 0.0258]	R_1 = 0.0848
	wR_2 = 0.1823	wR_2 = 0.0757	wR_2 = 0.0760	wR_2 = 0.0537	wR_2 = 0.1591
Largest difference in peak/hole, e Å^{-3}	1.998/−1.945	1.048/−0.671	1.594/−0.889	0.368/−0.469	0.713/−0.900

[a] $R_1 = \Sigma|F_o - F_c|/\Sigma|F_o|$ and $wR_2 = \Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2$.

A number of complexes of molybdenyl with aryl-substituted hydroxamic acids have been obtained by acidifying an aqueous solution of a mixture of appropriate proligand and sodium molybdate [23]. The increase in the hydrophobicity of proligands as a consequence of lengthening of hydroxamate grouping alkyl substituents (C_5H_{11}) necessitates the use of an aqueous-organic solvent to carry out synthesis analogous to the above one [24]. We have found that further increase of the mass of alkyl substituents (C_9H_{19}) necessitates considerable updating of the conditions for the synthesis of complexes in aqueous-organic media. To achieve acceptable homogenization of the reaction mixture at the beginning of synthesis, it is necessary to stir it vigorously and to adjust the pH value to no less than 12.0. When the reaction mixture is acidified to pH 3.0, an emulsion is formed, which crystallizes into the desired product only on long standing at 5 °C.

$$2HL + Na_2MoO_4 \xrightarrow[(pH\ 12;pH\ 3)]{+2HCl} MoO_2L_2 + 2NaCl + 2H_2O \quad (2)$$

Larson et al. isolated and described a stable adduct $MoO_2Cl_2{\cdot}2DMF$, which is readily soluble in a number of organic solvents [25]. We have found that 0.2 M solutions of MoO_2Cl_2 in dimethylformamide can keep (in absence of moisture, in the dark) several months without losing its suitability for the synthesis of molybdenyl hydroxamato complexes according to the scheme:

$$2HL + MoO_2Cl_2 \xrightarrow{2N(C_2H_5)_3} MoO_2L_2 + 2N(C_2H_5)_3 \cdot HCl \quad (3)$$

The acceptable solubility of the starting compounds, including hydroxamic acids, in the above solvent and the effective binding of hydrogen chloride, which evolves during reaction, by triethylamine ensure high yields of the desired products. The experimental technique which is employed in the syntheses of organolithium compounds is quite suitable for this method [26]. The method for the synthesis of molybdenum dioxydichloride (Eq. (4)) presented in this article is preparative and allows one to use this compound widely as a precursor in syntheses of Mo (VI) coordination compounds. The used stock is easily removed from the reactor and regenerated *via* ammonium paramolybdate to starting MoO_3.

$$2MoO_3 + 2NaCl \xrightarrow{600\ ^\circ C} MoO_2Cl_2 + Na_2MoO_4 \quad (4)$$

The method for the preparation of complex **4** differs greatly from the above procedures 1–3. We failed to isolate N-hexanoyl-O-benzoyl-N-*tert*-butylhydroxylamine as a chemically pure compound, though the synthesis was carried out by the procedure described for its closest analog [27]. The unpurified product obtained was used to synthesize hydroxamic acid by the procedure described for N-*tert*-butyl-benzohydroxamic acid [28]. Our attempts to purify N-*tert*-butyl-hexanohydroxamic acid by crystallization or by vacuum distillation (noticeable decomposition of the distillate) were unsuccessful. Therefore, the above hydroxamic acid was used, without isolating it in the pure state, as a precursor in the synthesis of complex **4**. The hydroxamic acids used in the synthesis of complexes **1**–**3**, **5** have been obtained as chemically pure compounds by known procedures. Since there are no spectroscopic data on the above compounds in the publications, we have characterized them by IR and ^1H NMR spectroscopy.

The data of the IR spectra of the compounds under investigation corroborate complex formation. In this case, the vibration frequencies of the C–O groups bonded to metal manifest themselves in the lower-frequency spectral region in comparison with the stretching vibration frequencies of the C=O groups of free hydroxamic acid (1660–1600 cm^{-1}, 1585 cm^{-1} for N-MAdHA). Besides, two intense characteristic vibrational bands of the *cis*-MoO_2 group in the range 945–880 cm^{-1} are observed in the spectra of complexes. In the high-frequency spectral region, the characteristic absorption band of stretching vibrations of the OH group (3250–3150 cm^{-1}) disappears on complex formation.

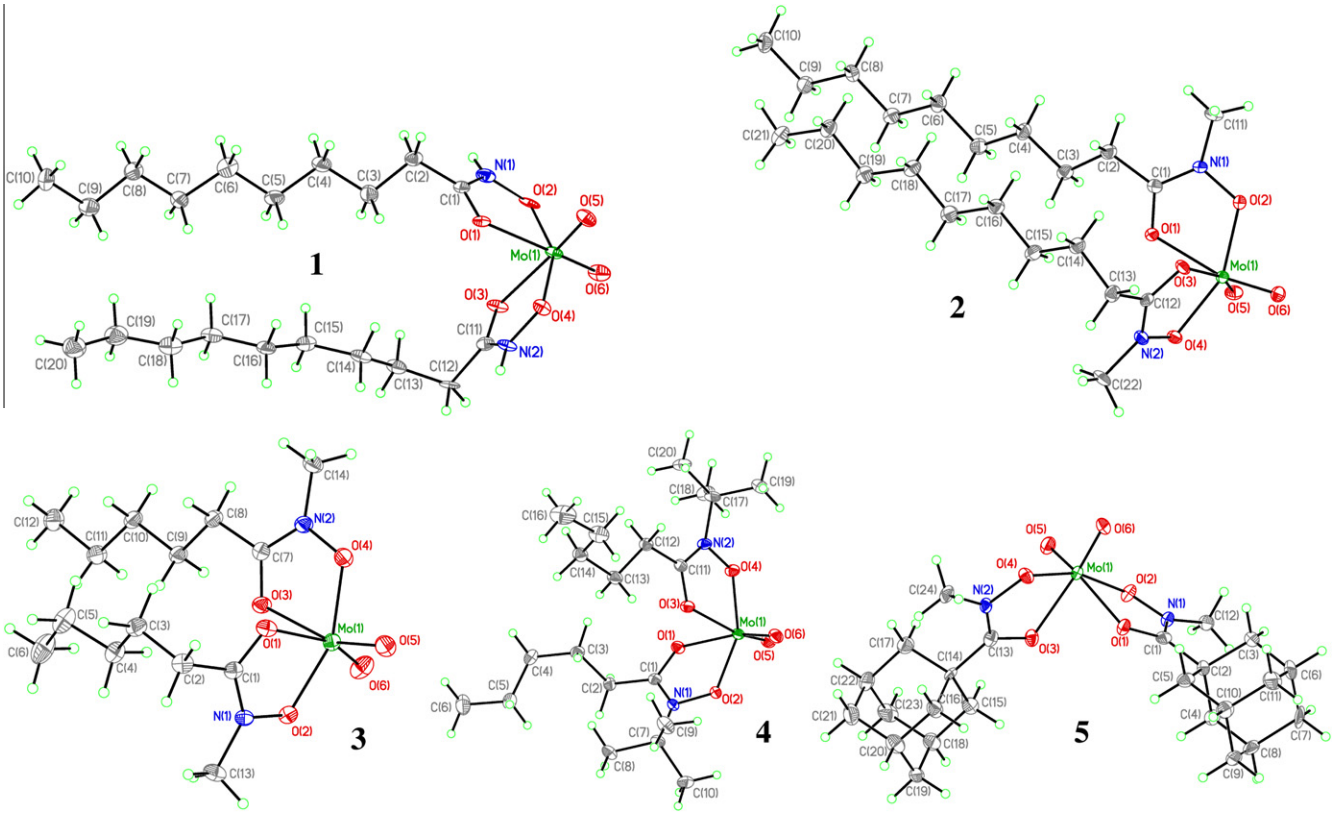


Fig. 1. The thermal ellipsoids plot of molecular structure of compounds **1**–**5**. The ellipsoids are shown at 50% probability level.

Table 2
Selected bond lengths and angles (Å) and (°).

	1	2	3	4	5
Mo(1)–O(1)	2.190(5)	2.2003(18)	2.1702(16)	2.1668(12)	2.177(4)
Mo(1)–O(2)	1.990(5)	1.9892(17)	2.0029(16)	1.9959(11)	2.007(3)
Mo(1)–O(3)	2.208(4)	2.1815(18)	2.1924(15)	2.1859(12)	2.193(4)
Mo(1)–O(4)	2.003(5)	1.9916(17)	2.0071(16)	1.9851(11)	2.002(3)
Mo(1)–O(5)	1.708(5)	1.7029(18)	1.7076(17)	1.7081(12)	1.705(4)
Mo(1)–O(6)	1.693(5)	1.6970(19)	1.6958(17)	1.7068(12)	1.701(4)
C(1)–O(1)	1.253(8)	1.268(3)	1.271(3)	1.274(2)	1.280(6)
C(1)–N(1)	1.310(9)	1.312(3)	1.317(3)	1.322(2)	1.337(6)
N(1)–O(2)	1.381(8)	1.387(3)	1.377(2)	1.3865(17)	1.359(5)
O(2)–Mo(1)–O(1)	74.43(18)	73.64(7)	73.26(6)	72.16(4)	72.48(14)
O(4)–Mo(1)–O(3)	73.98(17)	73.78(7)	73.37(6)	72.45(4)	72.30(14)
O(6)–Mo(1)–O(5)	105.8(2)	103.89(9)	104.34(9)	104.39(6)	105.26(19)

Table 3
Mean rms deviation from planes (Å) and dihedral angles between metal cycles (°) in **1–5**.

Compound	Plane	Rms deviation (Å)	Dihedral angle (°)
1	Mo(1)O(1)C(1)N(1)O(2)	0.0254	80.05(14)
	Mo(1)O(3)C(11)N(2)O(4)	0.0037	
2	Mo(1)O(1)C(1)N(1)O(2)	0.0367	72.38(6)
	Mo(1)O(3)C(12)N(2)O(4)	0.0343	
3	Mo(1)O(1)C(1)N(1)O(2)	0.0130	76.40(5)
	Mo(1)O(3)C(7)N(2)O(4)	0.0165	
4	Mo(1)O(1)C(1)N(1)O(2)	0.0761	74.31(3)
	Mo(1)O(3)C(11)N(2)O(4)	0.0236	
5	Mo(1)O(1)C(1)N(1)O(2)	0.0714	89.40(11)
	Mo(1)O(3)C(13)N(2)O(4)	0.0988	

The chemical shifts and integral intensities of signals in the ^{1}H NMR spectra of both molybdenyl complexes and free hydroxamic acid corroborate the above chemical structure (Scheme 1). In the solution of decanohydroxamic acid there are trace amounts of tautomeric E-keto form (9.71 ppm (NH) and 8.97 ppm (OH)) like what was revealed earlier for acetohydroxamic acid (the simplest homologue of DHA) in DMSO-d_6 solutions [29].

3.2. X-ray crystallography

The molecular structures of the investigated compounds **1–5** are shown in Fig. 1. The asymmetric units of all compounds, except **5**, contain one molecule of complex. Compound **5** crystallized with 2 independent molecules in asymmetric unit, which has similar geometrical parameters. For this reason, the discussion of the molecular structure of **5** will be based on the geometrical parameters of one of them. In spite of substituents with different electron donating properties near the hydroxamic nitrogen atom in the compounds **1–5**, their main values of geometrical parameters are very close together (Table 2). The Mo(1) atom shows strongly distorted octahedral geometry with the values of O–Mo–O angles in the range from 72.16(4)° to 105.8(2)° (Table 2). MoO_2^{2+} has a *cis*-configuration with Mo(1)–O(5) and Mo(1)–O(6) bond lengths around 1.70 Å in all investigated compounds, which corresponds to double bond (Mo=O) [30]. The angles O(5)–Mo(1)–O(6) for all complexes are very close to ideal tetrahedral ones, which can be accounted for by repulsive π–π interaction between O(5) and O(6). From the values of C(1)–O(1) and C(1)–N(1) bond lengths (Table 2) the π-delocalization of electron density between the O(1), C(1) and N(1) atoms can be identified [30]. The oxygen atoms O(1) and O(3) are in the *trans*-position to (Mo=O) double bonds, which cause an elongation of Mo(1)–O(1) and Mo(1)–O(3) relative to Mo(1)–O(2) and Mo(1)–O(4) of about 0.2 Å (Table 1). This fact is in good agreement with the previously published structures of related compounds [24] and can be accounted for by strong *trans*-effect of the (Mo=O) group. The metal cycles Mo(1)–O(1)–C(1)–N(1)–O(2) and Mo(1)–O(3)–C(X)–N(2)–O(4) (X = 11 for **1** and **4**; 12 for **2**; 7 for **3**; 13 for **5**) exhibit planar geometry. The mean rms deviations from planes and dihedral angles between metal cycles are given in Table 3. The dihedral angles for compounds **1–4**, which contain stereochemically labile hydrocarbon chains as a substituent near the carbonyl carbons, have values from 72.38(6)° to 80.05(14)° [24]. At the same time, the dihedral angle in **5** is near 90° (Table 3), which can be accounted for by bulky adamantyl substituent with the rigid cage structure near the carbonyl carbons in the molecule of complex.

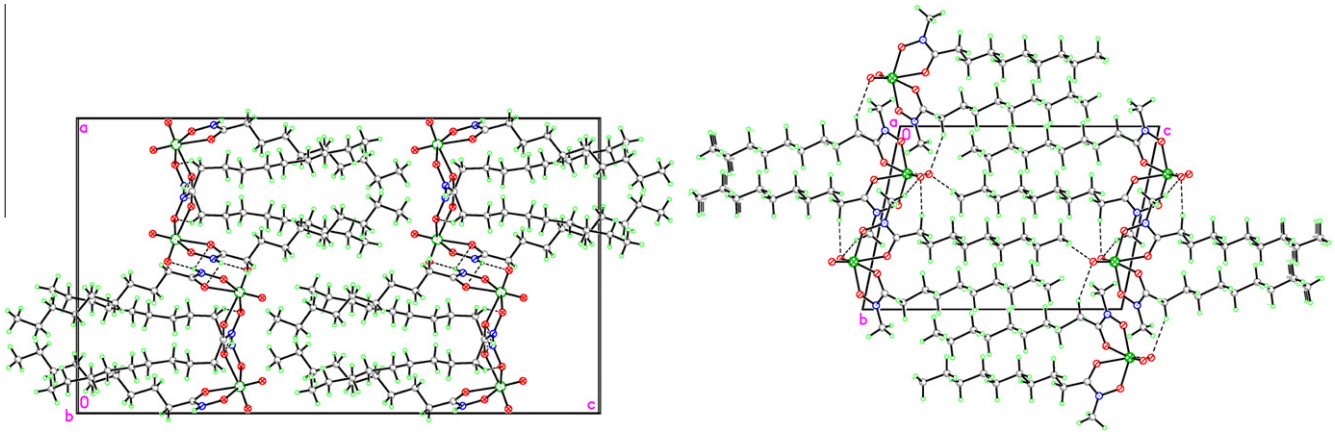


Fig. 2. Crystal packing projections for the compounds **1** (down the *b*-axis) and **2** (down the *a*-axis). The dashed lines indicate H-bonds.

Table 4
Hydrogen bonds for **1**.

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
N(1)–H(1N)···O(5)#1	0.85(4)	2.15(5)	2.973(8)	165(7)
N(2)–H(2N)···O(3)#2	0.92(4)	1.85(5)	2.741(7)	161(6)

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $y + 1/2$, $-z + 1/2$; #2 $-x + 1/2$, $y-1/2$, z.

Table 5
Hydrogen bonds for **2**.

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
C(2)–H(2A)···O(5)#1	0.99	2.35	3.328(3)	170.4
C(11)–H(11A)···O(5)#1	0.98	2.47	3.349(3)	148.4
C(10)–H(10B)···O(6)#2	0.98	2.46	3.422(4)	167.3
C(11)–H(11C)···O(2)#3	0.98	2.42	3.379(3)	166.7
C(13)–H(13B)···O(6)#4	0.99	2.57	3.413(3)	143.1

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1$, $-y + 1$, $-z + 2$; #2 $x + 1$, y, $z - 1$; #3 $-x$, $-y + 1$, $-z + 2$; #4 $-x$, $-y$, $-z + 2$.

The crystal structures of **1** and **2** exhibit a similar "head-to-tail" packing type in the 0 0 1 direction (Fig. 2). The chain of classical intermolecular N–H···O hydrogen bonds was found along 0 1 0 direction of the crystal structure **1** (Fig. 2; Table 4). It should be noted that even in dilute aqueous solutions, the complex of molybdenyl with acetohydroxamic acid (the simplest analog of $MoO_2(DH)_2$) forms intramolecular hydrogen bonds [31]. This may indicate a stable tendency of complexes of Mo (VI) with nitrogen-unsubstituted (N–H) hydroxamic acids to form hydrogen bonds. In $MoO_2(DH)_2$ crystals are formed so strong intermolecular hydrogen bonds that they make this compound (with long alkyl substituents) insoluble in ordinary solvents, such as chloroform and toluene.

In comparison with **1**, the crystal structure **2** displays much weaker intermolecular C–H···O contacts in the same direction (Fig. 2; Table 5). The difference in H-bond strength in the above structures has an effect on interplanar dihedral angles in investigated compounds (Table 2). The stronger N–H···O hydrogen bonds in **1** cause a significant increase in the dihedral angle between metal cycles relative to **2** of up to 7.5° (Table 2).

4. Conclusions

Thus, several methods for the synthesis of complexes of molybdenyl with hydrophobic alkyl-substituted hydroxamic acids have been developed. Taking into account the sufficient solubility of all parent compounds of the reaction mixture in aprotic polar solvent and the high yield of the desired products, the reaction between molybdenum dioxodichloride and appropriate hydroxamic acid in the presence of triethylamine in complete isolation from atmospheric moisture is the most acceptable. The preparative route to obtain MoO_2Cl_2 makes the above method readily accessible.

According to the data of X-ray diffraction analysis, the crystals of complexes **1–5** have an almost identical coordination polyhedron structure in spite of noticeable differences in the electron donating and steric properties of ligand substituents. The latter have an impact only on the values of dihedral angle between the planes of chelate rings. The presence of strong intermolecular hydrogen bonds in the complex $MoO_2(DH)_2$ affects greatly the decrease in the solubility of this compound in nonpolar organic solvents (decrease in lipophilicity) as compared with N-alkyl-substituted complexes.

In our view, the complexes described in this article can be useful as prototypes for the development of drugs based on lipophilic coordination compounds.

5. Supplementary data

CCDC 763211, 763213, 763212, 763210 and 763214 contains the supplementary crystallographic data for **1**, **2**, **3**, **4** and **5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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