

[RhCl(CO)(PPh₃)₂] (8 mg, 1.27 × 10⁻² mmol) was added to 1-pentyne (0.69 g, 10 mmol). This was followed by *t*-BuOOH (1.9 × 10⁻² mmol, 1.0 cm³ of 0.019 molar benzene solution). The mixture was allowed to stir at room temperature for 30 minutes, before triethylsilane (0.73 g, 6.3 mmol) was added. The solution was stirred at room temperature for 8 h. The yield and ratio of isomers were determined by quantitative g.l.c. on the Varian Aerograph 700 "Autoprep" Gas chromatograph using a 6 ft. column of 10% FFAP on Chromosorb G using indan as an internal standard.

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Ligand Function and Substrate Effect on Metal-Oxygen Stretching Frequencies in some *cis*-Dioxomolybdenum(VI) Complexes of Bivalent Tridentate Schiff Bases

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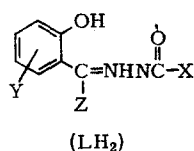
Summary

New dioxomolybdenum(VI) complexes [MoO₂LD] (LH₂ = Schiff base derived from isonicotinylhydrazide and salicylaldehyde, 2-hydroxynaphthaldehyde and 2-hydroxyacetophenone and benzoylhydrazide and 2-hydroxyacetophenone; D = H₂O, HCONMe₂, C₅H₅NO, C₄H₈O or Me₂SO) have been synthesized and characterized. The complexes contain a *cis*-MoO₂ moiety. The difference between ν_{sym} and ν_{asym} of MoO₂ is related to the basicity and ligand repulsion of the ligand (L) and the donor power of D. All the complexes decompose before melting and their thermal stability is in the order: C₄H₈O < HCONMe₂ < Me₂SO < C₅H₅NO < H₂O. The complexes are monomeric, non-electrolytes in solution in MeOH, MeCN and PhNO₂ and are diamagnetic.

Introduction

Of all the metals in 4d transition series, molybdenum has aroused considerable interest in recent years in view of its biochemical importance. It is an essential micronutrient for microorganisms, plants and animals⁽¹⁾. Schiff base complexes of first-row transition metals have been extensively investigated. Comparatively very little work has been reported on Schiff base complexes of molybdenum⁽¹⁻⁴⁾. The present paper deals with the preparation and characterization of some new dioxomolybdenum(VI) complexes of the type [MoO₂LD], with potential biantionic tridentate ligands (LH₂) and mono-

dentate oxygen donors D such as H₂O, dimethylformamide (DMF), pyridine *N*-oxide (PyO), tetrahydrofuran (THF) and dimethylsulphoxide (DMSO).



| | | |
|---------------------------------------|--------|---|
| Y = H | Z = H | X = C ₅ H ₄ N (INH ₂ ALH ₂) |
| Y = 5,6-C ₄ H ₄ | Z = H | X = C ₅ H ₄ N (INH ₂ NALH ₂) |
| Y = H | Z = Me | X = C ₅ H ₄ N (INH ₂ APH ₂) |
| Y = H | Z = Me | X = C ₆ H ₅ (BH ₂ APH ₂) |

Experimental

Reagents

Ammonium molybdate was supplied by May and Baker Ltd., England. Isonicotinylhydrazide, benzoylhydrazide and pyridine *N*-oxide from Koch Light Laboratories, England were used. 2-Hydroxyacetophenone was obtained from Boehringer, Ingelheim, West Germany. Salicylaldehyde, DMSO, DMF and THF were obtained from Sisco-Chem, Bombay, India. 2-Hydroxy-1-naphthaldehyde was prepared by the procedure given by Russel and Lockhart⁽⁵⁾.

Schiff bases were prepared by condensing carbonyl compounds with stoichiometric quantities of isonicotinylhydrazide or benzoylhydrazide in the usual way.

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Synthesis of [MoO₂L]

The complexes [MoO₂L(H₂O)] were prepared by adding dropwise with stirring a hot solution of ligand in EtOH (1 mmol in 50 cm³) to a hot aqueous solution of ammonium molybdate (1 mmol, 1.24 g in 150 cm³) at pH ca. 6.5. The stirring was continued for 30 min while heating, and the coloured precipitate formed was filtered, washed first with hot H₂O followed by Et₂O and dried *in vacuo* over P₄O₁₀. [MoO₂L(DMF)], [MoO₂L(DMSO)] and [MoO₂L(PyO)] were prepared by adding the oxygen donor in small quantities to a hot suspension of [MoO₂L(H₂O)] in dry C₆H₆ till the parent complex dissolved to give a clear solution. Petroleum ether

(40–60 °C) was added with stirring until the complex precipitated. The THF complexes were obtained by dissolving the aqua-complexes in the minimum of THF and precipitating the product with petroleum ether. The precipitated complexes were filtered, washed with petroleum ether and dried *in vacuo* over P₄O₁₀. The complexes are insoluble in H₂O and fairly or slightly soluble in almost all organic solvents. All of them decompose without melting.

Molybdenum was estimated gravimetrically as oxinate⁽⁶⁾. For this, the complexes were first decomposed with conc. H₂SO₄ and a few drops of HClO₄ to yield a clear and colourless solution. Using a Perkin-Elmer apparatus, the contents of the substances D were estimated by thermogravimetry. A typi-

Table 1. Colour, analytical, molecular weight and TG data of dioxomolybdenum(VI) complexes.

| Complex | Colour | Found (Calcd.)% | | Mol. wt. | Temp. range °C | | Second stage dec. | | Found (Calcd.)% | |
|---|-----------------|-----------------|----------------|------------------|------------------|------|-------------------|------|-----------------|----------------|
| | | Mo | D | | First stage dec. | From | To | From | To | Total wt. loss |
| [MoO ₂ (INHSAL)(H ₂ O)] C ₁₃ H ₁₁ N ₃ O ₅ Mo | orange-yellow | 24.6 (24.9) | 4.8 (4.7) | 376.8 (385.2) | 196 | 272 | 294 | 468 | 67.3 (62.6) | 32.7 (37.4) |
| [MoO ₂ (INHNAL)(H ₂ O)] C ₁₇ H ₁₃ N ₃ O ₅ Mo | red | 22.0 (22.0) | 4.0 (4.1) | 427.4 (435.3) | 261 | 303 | 310 | 470 | 68.0 (66.9) | 32.0 (33.0) |
| [MoO ₂ (INHAP)(H ₂ O)] C ₁₄ H ₁₃ N ₃ O ₅ Mo | yellow | 24.1 (24.0) | 4.6 (4.5) | 365.2 (399.2) | 212 | 305 | 309 | 513 | 63.0 (63.9) | 37.0 (36.0) |
| [MoO ₂ (BHAP)(H ₂ O)] C ₁₅ H ₁₄ N ₂ O ₅ Mo | light yellow | 24.1 (24.1) | 4.5 (4.5) | 367.4 (398.2) | 287 | 292 | 295 | 545 | 66.0 (63.8) | 34.0 (36.1) |
| [MoO ₂ (INHSAL)(PyO)] C ₁₈ H ₁₄ N ₄ O ₅ Mo | bright yellow | 20.3 (20.8) | 19.3 (20.5) | 448.6 (462.3) | 210 | 312 | 325 | 530 | 80.7 (68.9) | 19.3 (31.2) |
| [MoO ₂ (INHNAL)(PyO)] C ₂₂ H ₁₆ N ₄ O ₅ Mo | yellowish red | 18.5 (18.7) | 18.5 (18.6) | 545.0 (512.4) | 192 | 325 | 335 | 530 | 71.0 (71.9) | 28.9 (28.1) |
| [MoO ₂ (INHAP)(PyO)] C ₁₉ H ₁₆ N ₄ O ₅ Mo | bright yellow | 20.0 (20.1) | 19.8 (20.0) | 464.8 (476.3) | 150 | 275 | 295 | 540 | 65.4 (69.8) | 34.3 (30.2) |
| [MoO ₂ (BHAP)(PyO)] C ₂₀ H ₁₇ N ₃ O ₅ Mo | yellow | 20.2 (20.2) | 19.3 (20.0) | 467.0 (475.3) | 210 | 265 | 275 | 510 | 70.5 (69.7) | 29.0 (29.5) |
| [MoO ₂ (INHSAL)(DMF)] C ₁₆ H ₁₆ N ₄ O ₅ Mo | bright yellow | 21.0 (21.8) | 16.1 (16.6) | 449.2 (440.3) | 189 | 302 | 310 | 480 | 85.2 (67.3) | 14.8 (32.7) |
| [MoO ₂ (INHNAL)(DMF)] C ₁₇ H ₁₈ N ₄ O ₅ Mo | dark red | 19.4 (19.6) | 15.0 (14.9) | 494.6 (490.4) | 143 | 182 | 302 | 520 | 70.0 (70.6) | 30.0 (29.3) |
| [MoO ₂ (INHAP)(DMF)] C ₁₇ H ₁₈ N ₄ O ₅ Mo | bright yellow | 21.0 (21.1) | 15.4 (16.1) | 460.2 (454.3) | 142 | 296 | 307 | 550 | 65.4 (68.3) | 34.6 (31.6) |
| [MoO ₂ (BHAP)(DMF)] C ₁₈ H ₁₉ N ₃ O ₅ Mo | brownish yellow | 21.1 (21.2) | 15.5 (16.1) | 448.4 (453.3) | 172 | 282 | 292 | 540 | 64.7 (68.2) | 35.3 (31.8) |
| [MoO ₂ (INHSAL)(THF)] C ₁₇ H ₁₇ N ₃ O ₅ Mo | orange yellow | 21.1 (21.8) | 16.0 (16.4) | 427.3 (439.3) | 145 | 254 | 305 | 470 | 74.0 (67.2) | 26.0 (32.8) |
| [MoO ₂ (INHNAL)(THF)] C ₂₁ H ₁₉ N ₃ O ₅ Mo | yellowish red | 19.6 (19.6) | 15.2 (14.7) | 491.7 (489.3) | 126 | 326 | 332 | 485 | 70.7 (70.6) | 29.3 (29.4) |
| [MoO ₂ (INHAP)(THF)] C ₁₈ H ₁₉ N ₃ O ₅ Mo | bright yellow | 21.1 (21.2) | 17.8 (15.9) | 445.6 (453.3) | 133 | 300 | 326 | 520 | 67.8 (68.2) | 32.2 (31.8) |
| [MoO ₂ (BHAP)(THF)] C ₁₉ H ₂₀ N ₂ O ₅ Mo | brownish red | 21.2 (21.2) | 16.3 (15.9) | 464.8 (452.3) | 126 | 295 | 303 | 530 | 69.4 (68.2) | 30.6 (31.8) |
| [MoO ₂ (INHSAL)(DMSO)] C ₁₅ H ₁₅ N ₃ O ₅ SMo | orange yellow | 21.1 (21.6) | 16.8 (17.6) | 426.2 (445.3) | 181 | 317 | 329 | 482 | 80.0 (67.7) | 20.0 (32.3) |
| [MoO ₂ (INHNAL)(DMSO)] C ₁₉ H ₁₇ N ₃ O ₅ SMo | yellowish red | 19.3 (19.4) | 15.3 (15.8) | 501.0 (495.4) | 184 | 290 | 325 | 510 | 77.2 (70.9) | 22.6 (29.1) |
| [MoO ₂ (INHAP)(DMSO)] C ₁₆ H ₁₇ N ₃ O ₅ SMo | bright yellow | 20.6 (20.9) | 18.0 (17.0) | 455.1 (459.3) | 299 | 320 | 325 | 510 | 66.7 (68.7) | 33.3 (31.4) |
| [MoO ₂ (BHAP)(DMSO)] C ₁₇ H ₁₈ N ₂ O ₅ SMo | orange yellow | 21.0 (20.9) | 18.0 (17.1) | 463.0 (458.3) | 127 | 185 | 250 | 540 | 69.0 (68.6) | 31.0 (31.4) |

cal complex $[\text{MoO}_2(\text{INHSAL})(\text{H}_2\text{O})]$ was analysed by the Australian Microanalytical Service. (Found: C, 41.3; H, 3.0; N, 10.2. Calcd.: C, 40.5; H, 2.9; N, 10.9%.) Molecular weights were determined by Rast's method⁽⁷⁾, using biphenyl as solvent. Molar conductance in solvents such as methanol, acetonitrile and nitrobenzene and magnetic susceptibility measurements were made at room temperatures as described earlier⁽⁸⁾. I.r. spectra were recorded in KBr using a Perkin-Elmer 397 spectrophotometer.

Results and Discussion

The compounds analyse as $[\text{MoO}_2\text{LD}]$. The molecular weights correspond to monomers (Table 1). All are nonelec-

trolytes in solvents such as methanol, acetonitrile and nitrobenzene and are diamagnetic as expected.

The i.r. spectral data of the complexes are typical of coordinated anionic Schiff bases and oxygen donors (Table 2). The $\nu(\text{C}=\text{O})$ at $1640\text{--}1685\text{ cm}^{-1}$ of the Schiff bases disappears in complexes suggesting enolization of ligands and the reaction of the enol form with the metal with the elimination of a proton^(3, 4, 9). A new band in the complexes at $1260\text{--}1300\text{ cm}^{-1}$ may be due to the enolic $\nu(\text{C}-\text{O})$ ⁽⁴⁾. There is no $\nu(\text{N}-\text{H})$ in the spectra of the complexes⁽¹⁰⁾. No new $=\text{N}-\text{N}$ -stretching^(11, 12) bands were observed, but there are more intense bands of the *cis*- MoO_2 oxocation in the same region⁽¹³⁻¹⁵⁾. The complexes do not show phenolic $\nu(\text{OH})$ ⁽²⁾. The $\nu(\text{C}-\text{O})$ bands at

Table 2. I.r. spectral data of dioxomolybdenum(VI) complexes (cm^{-1}).

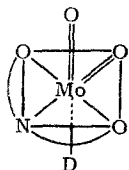
| Complex (Ligand) | $\nu(\text{C}=\text{N})$ | $\nu(\text{C}-\text{O})$ Phenolic | $\nu(\text{C}-\text{O})$ Enolic | ν_{sym} ($\text{O}=\text{Mo}=\text{O}$) | ν_{asymm} ($\text{O}=\text{Mo}=\text{O}$) | $\nu(\text{Mo}-\text{N})$ | $\nu(\text{Mo}-\text{O})$ | D bands | $\Delta \nu$ (MoO_2) ($\nu_{\text{sym}}-\nu_{\text{asymm}}$) |
|--|--------------------------|--------------------------------------|------------------------------------|---|---|---------------------------|---------------------------|---|--|
| $[\text{MoO}_2(\text{INHSAL})(\text{H}_2\text{O})]$ (INHSALH_2) ^a | 1595vs (1615)s | 1548s (1540)vs | 1260s | 922s | 898vs | 590m | 550w | 3450Sb, $-\nu(\text{OH})$ (H_2O) | 24 |
| $[\text{MoO}_2(\text{INHSAL})(\text{DMF})]$ (INHSALH_2) | 1600vs (1615)s | 1550s (1540)vs | 1260s | 932s | 908vs | 590m | 550w | 1650vs, $-\nu(\text{C}=\text{O})$ (1680)vs | 24 |
| $[\text{MoO}_2(\text{INHSAL})(\text{PyO})]$ (INHSALH_2) | 1595vs (1615)s | 1550s (1540)vs | 1260s | 926s | 904vs | 585s | 545m | 1195vs, $-\nu(\text{N}=\text{O})$ (1250)vs | 22 |
| $[\text{MoO}_2(\text{INHSAL})(\text{THF})]$ (INHSALH_2) | 1595vs (1615)s | 1550m (1540)vs | 1265s | 928s | 912vs | 590m | 555w | 1005m, $-\nu(\text{C}-\text{O}-\text{C})$ (1065)vs | 16 |
| $[\text{MoO}_2(\text{INHSAL})(\text{DMSO})]$ (INHSALH_2) | 1595vs (1615)s | 1550m (1540)vs | 1260s | 910s | 894vs | 590s | 555w | 1000m, $-\nu(\text{S}=\text{O})$ (1040)vs | 16 |
| $[\text{MoO}_2(\text{INHNAL})(\text{H}_2\text{O})]$ (INHNALH_2) ^b | 1595vs (1625)s | 1545s (1540)vs | 1275m | 928s | 902vs | 585s | 540w | 3450Sb, $-\nu(\text{OH})$ (H_2O) | 26 |
| $[\text{MoO}_2(\text{INHNAL})(\text{DMF})]$ (INHNALH_2) | 1595vs (1625)s | 1545s (1540)vs | 1275s | 924s | 898vs | 585s | 540w | 1640vs, $-\nu(\text{C}=\text{O})$ (1680)vs | 26 |
| $[\text{MoO}_2(\text{INHNAL})(\text{PyO})]$ (INHNALH_2) | 1595vs (1625)s | 1546s (1540)vs | 1275m | 920s | 898vs | 585s | 540w | 1210s, $-\nu(\text{N}=\text{O})$ (1250)vs | 22 |
| $[\text{MoO}_2(\text{INHNAL})(\text{THF})]$ (INHNALH_2) | 1595vs (1625)s | 1548s (1540)vs | 1275s | 930s | 908vs | 585s | 540w | 1005m, $-\nu(\text{C}-\text{O}-\text{C})$ (1065)vs | 22 |
| $[\text{MoO}_2(\text{INHNAL})(\text{DMSO})]$ (INHNALH_2) | 1595vs (1625)s | 1546s (1540)vs | 1275s | 918s | 900vs | 590s | 540w | 990m, $-\nu(\text{S}=\text{O})$ (1040)vs | 18 |
| $[\text{MoO}_2(\text{INHAP})(\text{H}_2\text{O})]$ (INHAPH_2) ^c | 1585vs (1605)vs | 1545s (1540)vs | 1300s | 934s | 908vs | 600m | 525w | 3375Sb, $-\nu(\text{OH})$ (H_2O) | 26 |
| $[\text{MoO}_2(\text{INHAP})(\text{DMF})]$ (INHAPH_2) | 1585vs (1605)vs | 1545s (1540)vs | 1295s | 930s | 904vs | 600s | 525w | 1665vs, $-\nu(\text{C}=\text{O})$ (1680)vs | 26 |
| $[\text{MoO}_2(\text{INHAP})(\text{PyO})]$ (INHAPH_2) | 1585vs (1605)vs | 1545s (1540)vs | 1295s | 926s | 900vs | 600s | 545m | 1200s, $-\nu(\text{N}=\text{O})$ (1250)vs | 26 |
| $[\text{MoO}_2(\text{INHAP})(\text{THF})]$ (INHAPH_2) | 1585vs (1606)vs | 1545s (1540)vs | 1300s | 932s | 908vs | 600m | 525w | 1010m, $-\nu(\text{C}-\text{O}-\text{C})$ (1065)vs | 24 |
| $[\text{MoO}_2(\text{INHAP})(\text{DMSO})]$ (INHAPH_2) | 1590vs (1605)vs | 1545s (1540)vs | 1300s | 930s | 906vs | 600s | 525m | 1010m, $-\nu(\text{S}=\text{O})$ (1040)vs | 24 |
| $[\text{MoO}_2(\text{BHAP})(\text{H}_2\text{O})]$ (BHAPH_2) ^d | 1605vs (1615)vs | 1555s (1525)vs | 1290s | 870s | 846vs | 580m | 520w | 3400sb, $-\nu(\text{OH})$ (H_2O) | 24 |
| $[\text{MoO}_2(\text{BHAP})(\text{DMF})]$ (BHAPH_2) | 1595vs (1615)vs | 1550s (1525)vs | 1290s | 906s | 894vs | 600m | 520w | 1640vs, $-\nu(\text{C}=\text{O})$ (1680)vs | 12 |
| $[\text{MoO}_2(\text{BHAP})(\text{PyO})]$ (BHAPH_2) | 1595vs (1615)vs | 1555s (1525)vs | 1295s | 908s | 896vs | 595s | 545m | 1200s, $-\nu(\text{N}=\text{O})$ (1250)vs | 12 |
| $[\text{MoO}_2(\text{BHAP})(\text{THF})]$ (BHAPH_2) | 1605vs (1615)vs | 1555s (1525)vs | 1290s | 870m | 848vs | 585m | 515w | 1020, $-\nu(\text{C}-\text{O}-\text{C})$ (1065)vs | 22 |
| $[\text{MoO}_2(\text{BHAP})(\text{DMSO})]$ (BHAPH_2) | 1595vs (1615)vs | 1550s (1525)vs | 1290s | 908s | 898vs | 600s | 520w | 990s, $-\nu(\text{S}=\text{O})$ (1040)vs | 10 |

^a $\nu(\text{N}-\text{H})$ 3175Sb; $\nu(\text{OH}, \text{phenolic})$ 3000sb; $\nu(\text{C}=\text{O})$ 1685vs; ^b $\nu(\text{N}-\text{H})$ 3200mb; $\nu(\text{OH}, \text{phenolic})$ 3030mb; $\nu(\text{C}=\text{O})$ 1675vs; ^c $\nu(\text{N}-\text{H})$ 3100mb; $\nu(\text{OH}, \text{phenolic})$ 2950mb; $\nu(\text{C}=\text{O})$ 1670vs; ^d $\nu(\text{N}-\text{H})$ 3200sb; $\nu(\text{OH}, \text{phenolic})$ 3000mb; $\nu(\text{C}=\text{O})$ 1660vs and 1640vs.

1525–1540 cm⁻¹ of the ligands shift to higher frequencies by 5–30 cm⁻¹. These are all suggestive of the coordination of phenolic C–O groups^(3, 4, 9). The $\nu(\text{C}=\text{N})$ at 1605–1625 cm⁻¹ of the ligands exhibit a negative shift of 10–30 cm⁻¹ in the complexes and this indicates the coordination of azomethine nitrogen to molybdenum^(3, 4, 9). Bands at 585–600 and 515–555 cm⁻¹, respectively^(2, 13, 16) are assigned to $\nu(\text{Mo}-\text{N})$ and $\nu(\text{Mo}-\text{O})$. Thus the i.r. data suggest bivalent tridentate ONO donor behaviour for the ligands L.

The broad bands at 3375–3450 cm⁻¹ in the spectra of $[\text{MoO}_2\text{L}(\text{H}_2\text{O})]$ are due to $\nu(\text{OH})$ of coordinated H₂O^(3, 4). The water was retained even on heating to a temperature of 120 °C for several hours. Negative shifts of 15–40, 45–50, 40–60 and 40–50 cm⁻¹ from 1675, 1250, 1065 and 1040 cm⁻¹ exhibited by $\nu(\text{X}=\text{O})$ of DMF^(17–19), PyO⁽¹⁷⁾ and DMSO⁽¹⁷⁾ and $\nu_{\text{asymm}}(\text{C}-\text{O}-\text{C})$ of THF⁽³⁾, respectively, are suggestive of their coordination through oxygen atoms.

The tendency of MoO₂²⁺ to form a *cis*-configuration is well established, and is attributed to the maximum utilization of the available d π orbitals for bonding with the oxo-groups⁽²⁰⁾. Dioxomolybdenum(VI) complexes with a *cis*-MoO₂ moiety exhibit two strong bands at 905–948 and 875–914 cm⁻¹ assignable to the $\nu_{\text{symm}}(\text{O}=\text{Mo}=\text{O})$ and $\nu_{\text{asymm}}(\text{O}=\text{Mo}=\text{O})$, respectively^(13–15). A *trans*-MoO₂ species would show only one i.r.-active band. All the complexes exhibit bands in the regions 870–934 and 848–908 cm⁻¹ indicating the presence of a *cis*-MoO₂ moiety. On the basis of the evidence presented here, the following structure is proposed for the complexes.



It is interesting to note that the separation between the ν_{symm} and ν_{asymm} ($\Delta\nu$) decreases in the following order for the ligands; L: INHAP > INHNAL > INHSAL > BHAP. For the ligand D it increases in the following order: DMSO < THF < PyO < DMF < H₂O. This parallels changes in $\nu(\text{C}=\text{N})$ and phenolic $\nu(\text{C}-\text{O})$ of the complexes, which decreases with increase in $\Delta\nu$ as L changes. Neither $\nu(\text{C}=\text{N})$ nor $\nu(\text{C}-\text{O})$ change with D.

Thermogravimetric studies show that the complexes $[\text{MoO}_2\text{LD}]$ decompose in two well defined stages leaving a

final residue approximating to MoO₃. The elimination of D from the complexes is found to occur at a temperature lower than the boiling point of D in some cases. Weight loss in the first stage (126–326 °C) corresponds to the quantitative elimination of D, and the second stage (250–550 °C) shows the decomposition of the complex to MoO₃. Lower values for the final residue are observed in the cases of $[\text{MoO}_2(\text{INHSAL})\text{D}]$. Independent pyrolysis experiments at ca. 550 °C show that all the complexes except $[\text{MoO}_2(\text{INHSAL})\text{D}]$ yield quantitatively MoO₃ as the final residue. $[\text{MoO}_2(\text{INHSAL})\text{D}]$ always gives varying lower weights of residue.

Work on different D and with various L is in progress.

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