2. EXPERIMENTAL METHODOLOGY

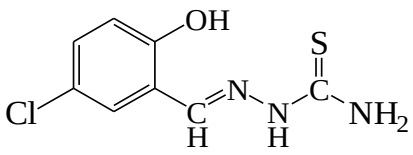
2.1 Synthesis

The following commercial chemicals of reagent grade quality were used in the synthesis: ammonium molybdate, acetylacetone, 5-chlorosalicylaldehyde, 3-ethoxysalicylaldehyde, 3,5-dichlorosalicylaldehyde, 4-hydroxysalicylaldehyde, thiosemicarbazide, 2-ethylthiosemi-carbazide, N-phenylthiosemicarbazide, 3-methoxybenzoic hydrazone (*m*-anisic hydrazide), 2-furoic hydrazide, 2,4-dihydroxybenzoic hydrazide, salicylaldehyde hydrazide, adipic acid dihydrazide, 4,4-bipyridine, 4,4-bipyridine N,N'-dioxide, tetramethylene sulfoxide, hexamethylphosphoramide, imidazole and concentrated nitric acid.

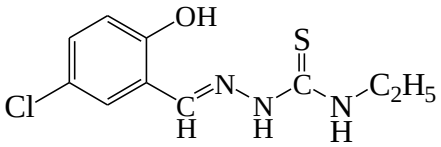
The solvents used in the preparation of Schiff base ligands and dioxomolybdenum(VI) complexes are methanol, ethanol, acetonitrile, dimethylsulfoxide, dimethylformamide and dichloromethane. These solvents are used without further purification. Structural formula, molecular formula, molecular weight and identification code for the ligands and complexes are listed in Scheme 1.

Scheme 1: Structural Formula For The Ligands and Molybdenum Complexes

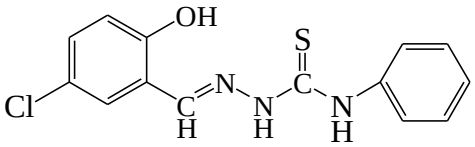
L1: 5-Chlorosalicylaldehyde thiosemicarbazone, $C_8H_8O_1N_3SCl$ *(229.5)*



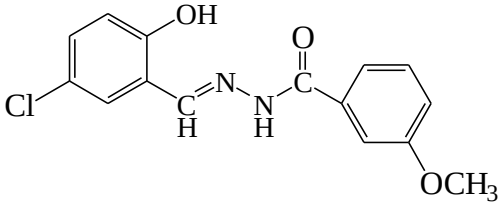
L2: 5-Chlorosalicylaldehyde 2-ethylthiosemicarbazone, *$C_{10}H_{12}O_1N_3SCl$ (257.5)*



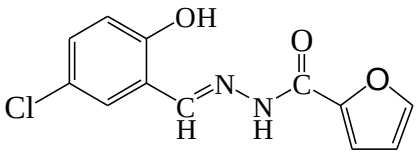
L3: 5-Chlorosalicylaldehyde N-phenylthiosemicarbazone, *$C_{14}H_{12}O_1N_3SCl$ (305.5)*



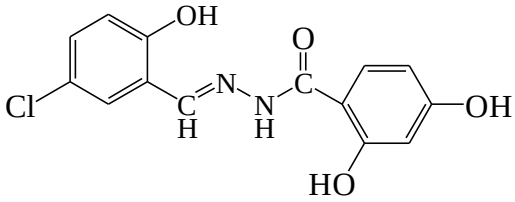
L4: 5-Chlorosalicylaldehyde 3-methoxybenzoic hydrazone, *$C_{15}H_{13}O_3N_2Cl$ (304.5)*



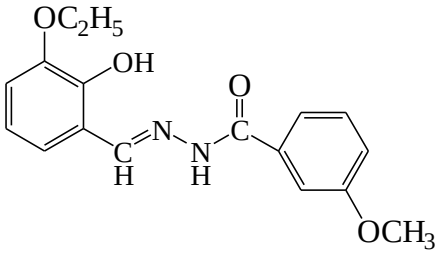
L5: 5-Chlorosalicylaldehyde 2-furyl hydrazone, *$C_{11}H_9O_3N_2Cl$ (252.5)*



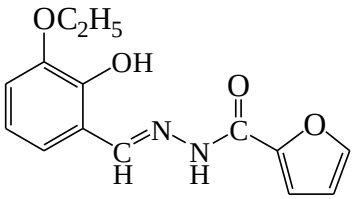
L6: 5-Chlorosalicylaldehyde 2,4-dihydroxybenzoic hydrazone, *$C_{14}H_{11}O_4N_2Cl$ (307.5)*



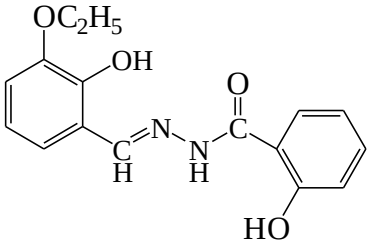
L7: 3- Ethoxysalicylaldehyde 3-methoxybenzoic hydrazone, *$C_{16}H_{18}O_4N_2$ (302)*



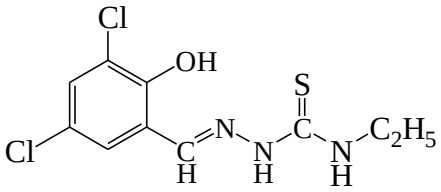
L8: 3- Ethoxysalicylaldehyde 2-furyl hydrazone, *$C_{14}H_{14}O_4N_2$ (274)*



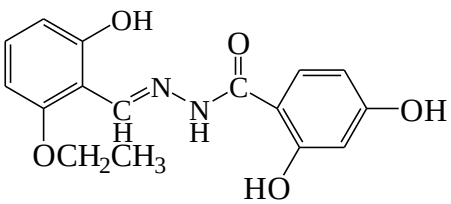
L9: 3- Ethoxysalicylaldehyde salicylhydrazone, *$C_{16}H_{16}O_4N_2$ (300)*



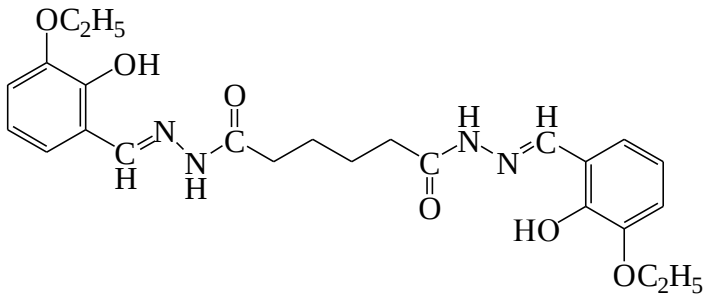
L10: 3,5-dichlorosalicylaldehyde 2-ethylthiosemicarbazone, *$C_{10}H_{12}O_3N_3SCl_2$ (293)*



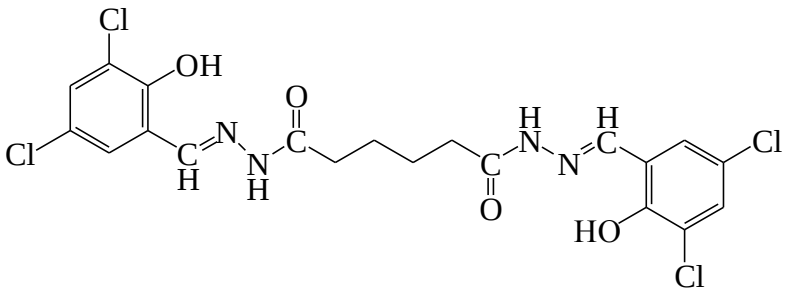
L11: 3-Ethoxysalicylaldehyde 2,4-dihydroxybenzoic hydrazone, *$C_{16}H_{16}O_5N_2$ (317)*



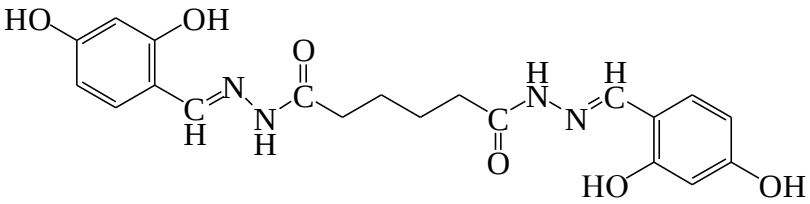
L12: 1,4-bis(3-ethoxysalicylaldehyde carbohydrazone) butane, *$C_{24}H_{30}O_4N_4$ (438)*



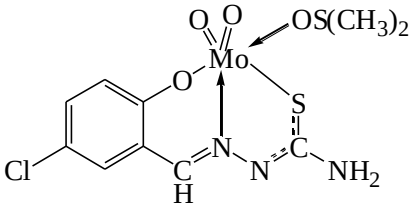
L13: 1,4-bis(3,5-dichlorosalicylaldehyde carbohydrazone) butane, *$C_{20}H_{18}O_4N_4Cl_4$ (449)*



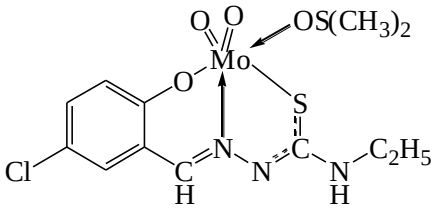
L14: 1,4-bis(4-hydroxysalicylaldehyde carbohydrazone) butane, *$C_{20}H_{22}O_6N_4$(414)*



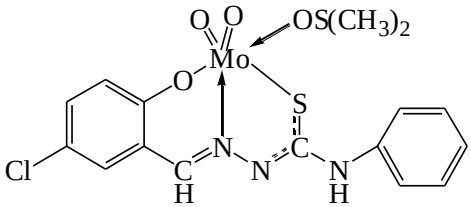
C1: [5-Chlorosalicylaldehyde thiosemicarbazonato](dimethylsulfoxide) dioxomolybdenum(VI) *$C_{10}H_{12}O_4N_3ClS_2Mo$ (433.5)*



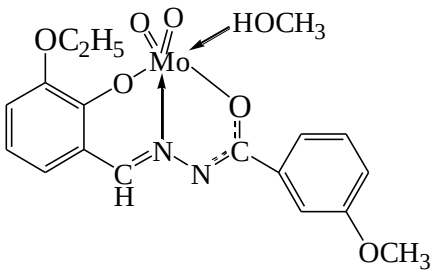
C2: [5-Chlorosalicylaldehyde 2-ethylthiosemicarbazonato](dimethylsulfoxide) dioxomolybdenum(VI) *$C_{12}H_{16}O_4N_3ClS_2Mo$ (461.5)*



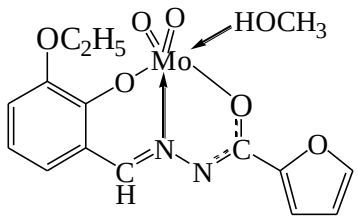
C3: [5-Chlorosalicylaldehyde *N*-phenylthiosemicarbazonato](dimethylsulfoxide) dioxomolybdenum(VI) *$C_{16}H_{16}O_4N_3ClS_2Mo$(509.5)*



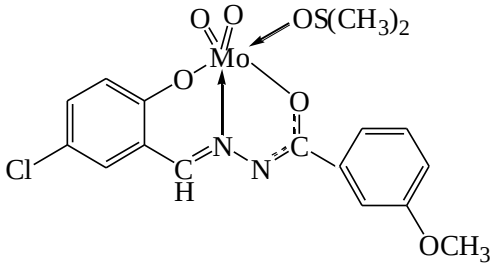
C4: [3-Ethoxysalicylaldehyde 3-methoxybenzoic hydrazonato](methanol) dioxomolybdenum(VI). *$C_{18}H_{20}O_7N_2Mo$(472)*



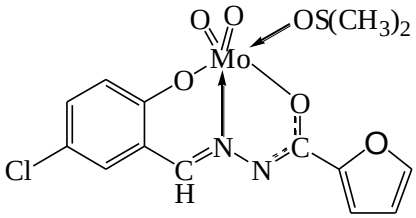
C5: [3-Ethoxysalicylaldehyde 2-furyl hydrazonato](methanol) dioxomolybdenum(VI) *$C_{15}H_{16}O_7N_2Mo(432)$*



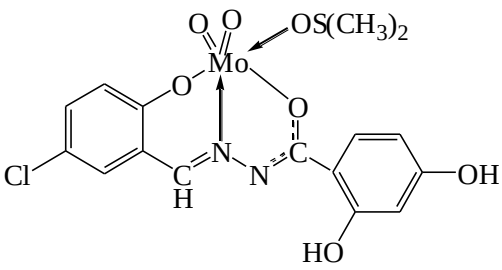
C6: [5-Chlorosalicylaldehyde 3-methoxybenzoic hydrazonato](dimethylsulfoxide) dioxomolybdenum(VI) *$C_{17}H_{17}O_6N_2ClSMo(508.5)$*



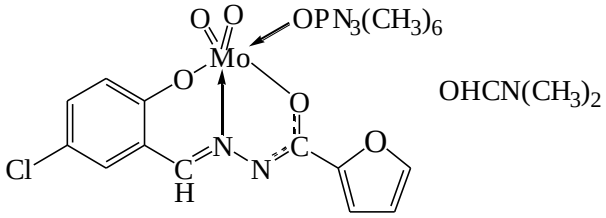
C7: [5-Chlorosalicylaldehyde 2-furyl hydrazonato](dimethylsulfoxide) dioxomolybdenum(VI) *$C_{14}H_{13}O_6N_2ClSMo(468.5)$*



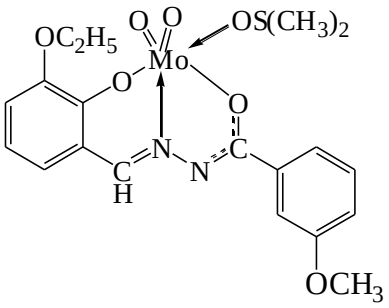
C8: [5-Chlorosalicylaldehyde 2,4-dihydroxybenzoic hydrazonato](dimethylsulfoxide) dioxomolybdenum(VI) *$C_{16}H_{15}O_7N_2ClSMo(510.5)$*



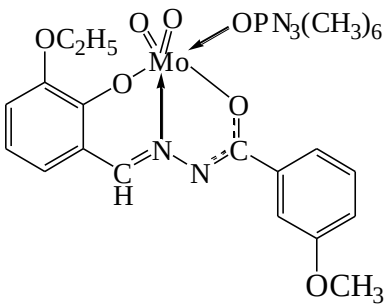
C9: [5-Chlorosalicylaldehyde 2-furyl hydrazonato](hexamethylphosphoramide) dioxomolybdenum(VI) dimethylformamide solvate *$C_{21}H_{30}O_7N_6ClPMo$ (636.5)*



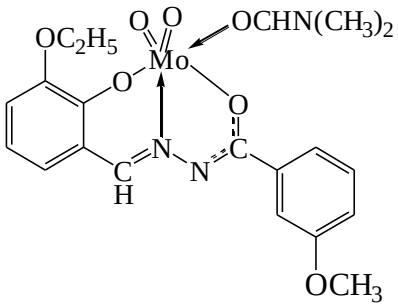
C10: [3-Ethoxysalicylaldehyde 3-methoxybenzoic hydrazonato](dimethylsulfoxide) dioxomolybdenum(VI) *$C_{19}H_{22}O_7N_2SMo(518)$*



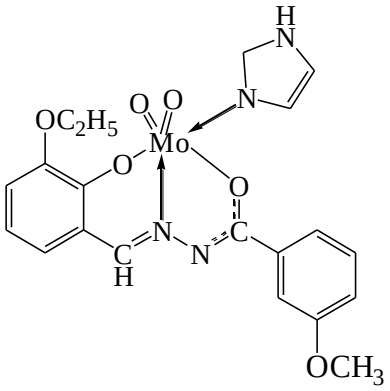
C11:[3-Ethoxysalicylaldehyde3-methoxybenzoic hydrazonato](hexamethylphosphoramide) dioxomolybdenum(VI) *$C_{23}H_{34}O_7N_5PMo(619)$*



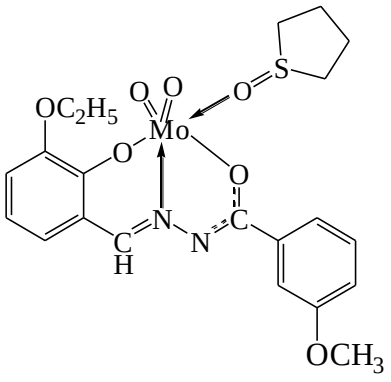
C12: [3-Ethoxysalicylaldehyde 3-methoxybenzoic hydrazonato](dimethylformamide) dioxomolybdenum(VI) *$C_{20}H_{23}O_7N_3Mo(513)$*



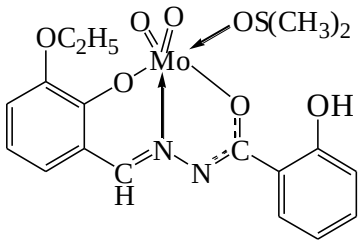
C13: [3-Ethoxysalicylaldehyde 3-methoxybenzoic hydrazonato](imidazole) dioxomolybdenum(VI) methanol solvate *$C_{21}H_{23}O_7N_4Mo(539)$*



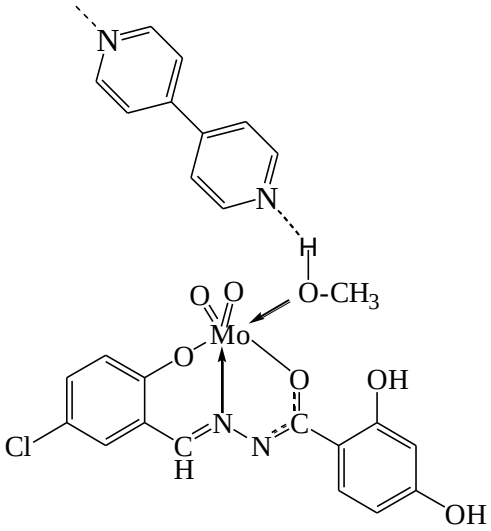
C14: [3-Ethoxysalicylaldehyde 3-methoxybenzoic hydrazonato](tetramethylene sulfoxide) dioxomolybdenum(VI) *$C_{21}H_{24}O_7N_2SMo(544)$*



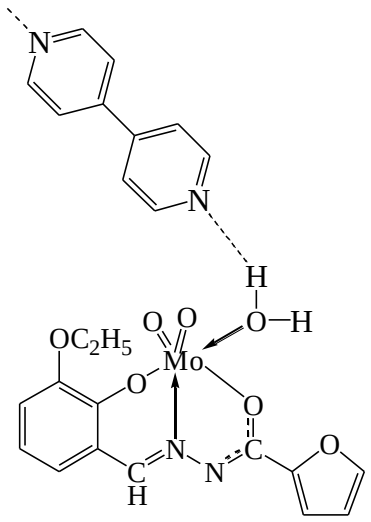
C15: [3-Ethoxysalicylaldehyde salicylhydrazonato](dimethylsulfoxide) dioxomolybdenum(VI) *$C_{18}H_{20}O_7N_2SMo(504)$*



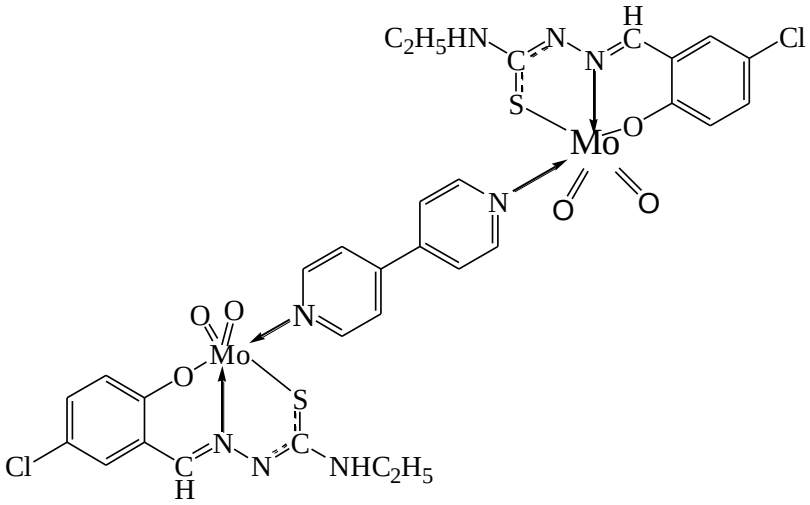
C16: [5-Chlorosalicylaldehyde 2,4-dihydroxybenzoic hydrazonato](methanol) dioxomolybdenum(VI) 4,4-bipyridine solvate *$C_{25}H_{21}O_7N_4ClMo(620.5)$*



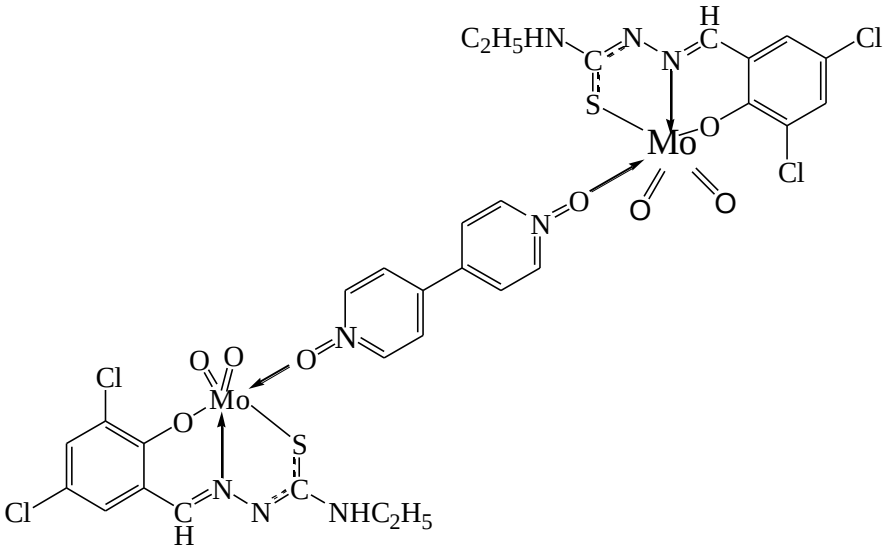
C17: [3-Ethoxysalicylaldehyde 2-furyl hydrazonato] aqua dioxomolybdenum(VI) 4,4-bipyridine solvate *$C_{24}H_{20}O_7N_4Mo(572)$*



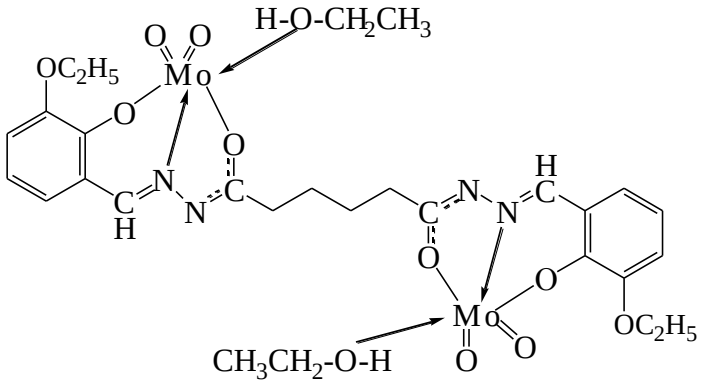
C18: (μ_2-4,4-Bipyridyl)-bis[(5-chlorosalicylaldehyde 2-ethylthiosemicarbazonato) dioxomolybdenum(VI) *$C_{30}H_{28}O_6N_8Cl_2S_2Mo_2$(923)*



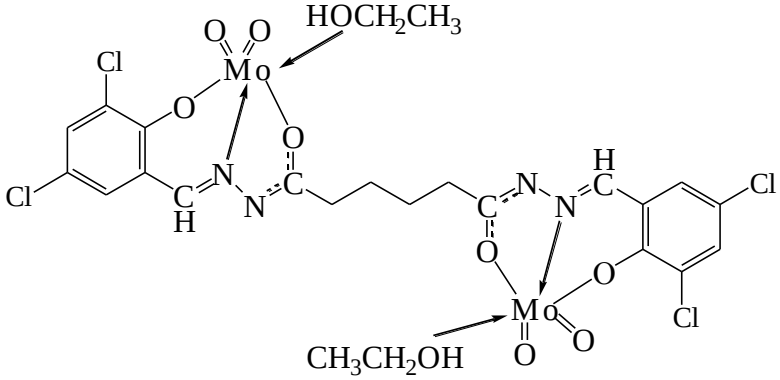
C19: (μ_2-4,4-Bipyridyl *N,N'*-dioxide)-bis[3,5-dichlorosalicylaldehyde 2-ethylthiosemicarbazonato) dioxomolybdenum(VI)] *$C_{30}H_{26}O_8N_8Cl_4S_2Mo_2$(1024)*



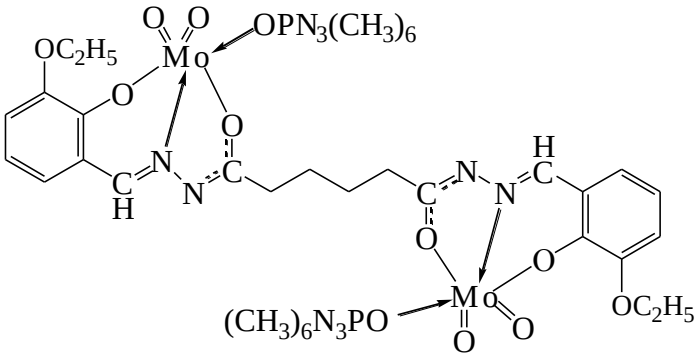
C20:1,4-Bis[(3-ethoxysalicylaldehyde carbohydrazonato)(ethanol) dioxomolybdenum(VI)] Butane *$C_{28}H_{38}O_{12}N_4\,Mo_2$(814)*



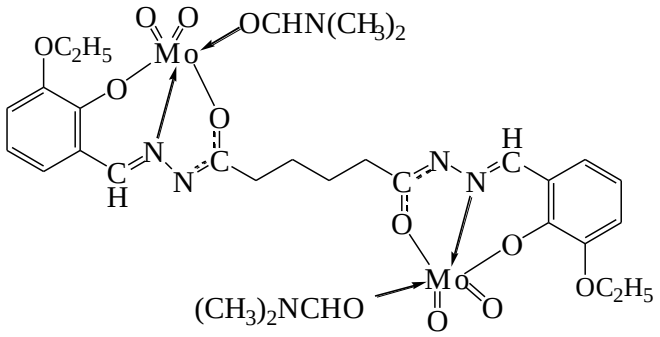
C21: 1,4-Bis[(3,5-dichlorosalicylaldehyde carbohydrazonato)(ethanol) dioxomolybdenum(VI)] butane *$C_{22}H_{28}O_{10}N_4\,Cl_2\,Mo_2$(866)*



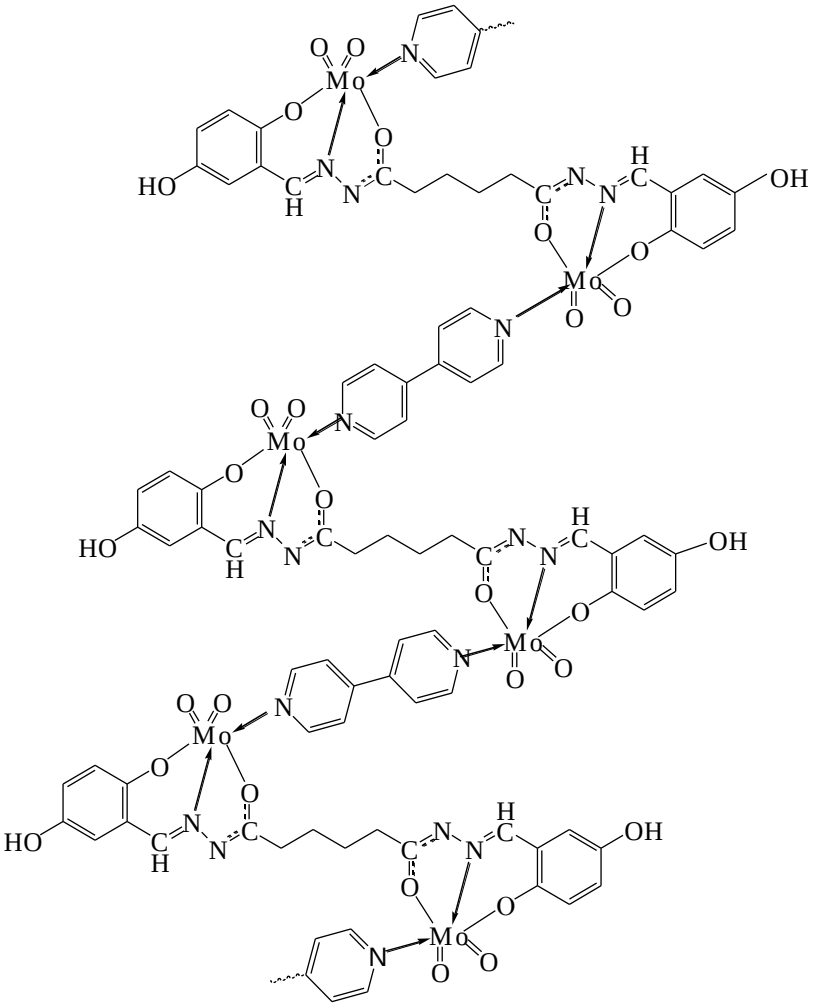
C22: 1,4-Bis[(3-ethoxysalicylaldehyde carbohydrazonato)(hexamethylphosphoramide) dioxomolybdenum(VI)] butane *$C_{36}H_{62}O_{12}N_{10}\,P_2\,Mo_2$(1082)*



C23: 1,4-Bis[(3-ethoxysalicylaldehyde carbohydrazonato)(dimethylformamide) dioxomolybdenum(VI)] butane $C_{30}H_{40}O_{12}N_6Mo_2$*(868)*



C24: (μ_2-4,4-Bipyridyl)-bis[1,4-(4-hydroxysalicylaldehyde carbohydrazonato) dioxomolybdenum(VI)]butane-methanol solvate, $[C_{15}H_{17}O_5N_3Mo]_n$ *(445)*



The value in parentheses at the end of each compound name refers to the theoretical molecular weight.

2.2 Physical Measurement

Melting Points

The melting points of the compounds were determined on a Melt-Temp apparatus and were uncorrected.

Elemental Analyses

Elemental analysis was performed at the in-house microanalytical laboratory using a Perkin-Elmer 2400 Series II CHNS/O System.

Infra Red (IR)

IR spectra were recorded in the range of 4000 – 400 cm^{-1} by using a Perkin-Elmer Spectrum 2000 FT-IR Spectrophotometer and Perkin Elmer Spectrum RX1 FT-IR Spectrophotometer. The sample were prepared either as nujol mulls or KBr pellet.

Nuclear Magnetic Resonance (NMR)

^{1}H and ^{13}C NMR spectra of the ligands and complexes were measured in DMSO-d_6 at ambient temperature on a JEOL Lambda 400 FT-NMR SYSTEM Spectrometer operating at 399.65 MHz for ^{1}H and and 100.40 MHz for ^{13}C NMR and on a ECA 400 MHz NMR spectrometers.

UV-Visible

Electronic absorption spectral measurement of the ligands and complexes in DMF were measured using Shimadzu-1650-PC-UV-vis spectrophotometer and were scanned from 200 – 800 nm.

Thermogravimetric Analysis

Thermal analysis (TGA) of the complexes was carried out by heating in nitrogen gas at a rate of 20^{o}C per minute on a Perkin Elmer TGA- 4000 thermo balance.

Cyclic Voltammetry Analysis

Cyclic voltammetry was carried out using Methrohm Autolab B.V. model. The measurements were done in DMF solution containing 0.1 M TEAP as supporting electrolyte and $5x10^{-4}$ M complex solution deoxygenated by bubbling with nitrogen gas. The working, counter and reference electrodes used were Pt wire, platinum coil and SCE, respectively.

X-ray Crystallographic Data Collection

The X-ray crystallographic intensity data were measured using Mo-Kα radiation (graphite crystal monochromator, λ = 0.71069 Å). The data collection was done at 296 K on an Bruker APEX II with a CCD area-detector X-ray diffractometer. The structures were solved by direct method with the SHELXS97 program and refined on F^2 by full-matrix least-squares methods with anisotropic non-hydrogen atoms.

2.3 Preparation Of Mononucleating Ligands

General procedures

All the Schiff base ligands **L1** to **L11** were prepared by the condensation reactions of 5-chlorosalicylaldehyde, 3-ethoxysalicylaldehyde, 3,5-dichlorosalicylaldehyde and 4-hydrox-salicylaldehyde with thiosemicarbazide, 2-ethylthiosemicarbazide, N-phenylthiosemi-carbazide, *3*-methoxybenzoichydrazide, 2-furoic hydrazide, 2,4 dihydroxy-benzoic hydrazide or salicylhydrazide in 1:1 ratio, respectively.

***Synthesis 5-Chlorosalicylaldehyde thiosemicarbazone* (L1)**

0.156 g (1.0 mmol) of 5-chlorosalicylaldehyde in 20 ml methanol was added to 20 ml solution of 0.091 g (1.0 mmol) of thiosemicarbazide. The solution mixture was refluxed with vigorous stirring for 2 hours and the colour of the solution changed from colourless to yellow. The resulting yellow solution was then filtered and allowed to stand at room temperature during which the yellow precipitate were formed. The precipitates were filtered and washed with methanol and dried in air. The ligand was used without further purification. *M.p.: 220-222^{o}C, (0.25 g, 71 %) Calcd. for $C_8H_8N_3OClS$: C, 41.74; H, 3.48; N, 18.26; S, 13.91%; Found: C, 42.03; H, 3.44; N, 17.88; S, 14.18%.*

***Synthesis of 5-Chlorosalicylaldehyde 2-ethylthiosemicarbazone* (L2)**

0.156 g (1.0 mmol) of 5-chlorosalicylaldehyde in 20 ml methanol was added to 20 ml solution of 0.120 g (1.0 mmol) of 2-ethylthiosemicarbazide. The solution mixture was refluxed with vigorous stirring for 2 hours. The resulting solution was then filtered and allowed to stand at room temperature during which the pale yellow solid was formed. The precipitates were filtered and washed with methanol and dried in air. The ligand was used

without further purification. *M.p.: 150-153^{o}C, (0.23 g, 68 %) Calcd. for $C_{10}H_{12}N_3OClS$: C, 46.69; H, 4.67; N, 16.34; S, 12.40%; Found: C, 47.11; H, 3.80; N, 15.95; S, 12.12%.*

Synthesis of 5-Chlorosalicylaldehyde N-phenylthiosemicarbazone **(L3)**

0.156 g (1.0 mmol) of 5-chlorosalicylaldehyde in 20 ml methanol was added to 20 ml solution of 0.167 g (1.0 mmol) of N-phenylthiosemicarbazide. The solution mixture was refluxed with vigorous stirring for 2 hours. The resulting solution was then filtered and allowed to stand at room temperature. Yellow crystals were formed during slow evaporation process. The crystals were collected and washed with methanol and dried in air. The ligand was used without further purification. *M.p.: 164-166^{o}C, (0.19 g, 57 %) Calcd. for $C_{14}H_{12}N_3OClS$: C, 54.90; H, 3.92; N, 13,73; S, 10.46%; Found: C, 55.17; H, 3.85; N, 14.13; S, 10.21%.*

Synthesis of 5-Chlorosalicylaldehyde 3-methoxybenzoic hydrazone **(L4)**

0.156 g (1.0 mmol) of 5-chlorosalicylaldehyde in 20 ml methanol was added to a 20 ml hot stirring methanolic solution of 0.166 g (1.0 mmol) of 3-methoxybenzoic hydrazide. The solution mixture was refluxed for 2 hours. The resulting solution was then filtered and allowed to stand at room temperature during which the white solid was formed. The solid was washed with methanol and dried in air. The ligand was used without further purification. *M.p.: 134-136^{o}C, (0.22 g, 64 %) Calcd. for $C_{15}H_{13}N_2O_3Cl$: C, 59.01; H, 4.25; N, 9.81%; Found: C, 60.18; H, 4.12; N, 9.95%.*

Syhthesis of 5-Chlorosalicylaldehyde 2-furylhydrazone **(L5)**

0.156 g (1.0 mmol) of 5-chlorosalicylaldehyde in 20 ml methanol was added to a 20 ml hot stirring methanolic solution of 0.126 g (1.0 mmol) of 2-furoic hydrazide. The solution mixture was refluxed for 2 hours. The resulting solution was then filtered and allowed to stand at room temperature during which the white solid was formed. The solid was washed with methanol and dried in air. The ligand was used without further purification. *M.p.: 154-156^{o}C, (0.17 g, 46 %) Calcd. for $C_{11}H_9N_2O_3Cl$: C, 52.38; H, 3.57; N, 11.11%; Found: C, 51.77; H, 3.12; N, 11.50%.*

Synthesis of 5-Chlorosalicylaldehyde 2,4-dihydroxybenzoic hydrazone **(L6)**

0.156 g (1.0 mmol) of 5-chlorosalicylaldehyde in 20 ml methanol was added to a 20 ml hot stirring methanolic solution of 0.168 g (1.0 mmol) of 2,4-dihydroxybenzoic hydrazide. The solution mixture was refluxed for 2 hours. The resulting solution was then filtered and allowed to stand at room temperature during which the white precipitates were formed. The precipitates were washed with methanol and dried in air. The ligand was used without further purification. *M.p.: 276-278^{o}C, (0.16g, 49 %) Calcd. for $C_{14}H_{11}N_2O_4Cl$: C, 54.55; H, 3.57; N, 9.09%; Found: C, 53.90; H, 3.22; N, 8.67%.*

Synthesis of 3-ethoxysalicylaldehyde 3-methoxybenzoic hydrazone **(L7)**

0.166 g (1.0 mmol) of 3-ethoxysalicylaldehyde in 20 ml methanol was added to a 20 ml hot stirring methanolic solution of 0.166 g (1.0 mmol) of 3-methoxybenzoic hydrazide. The solution mixture was refluxed for 2 hours. The yellowish reaction mixture became cloudy. The resulting solution was then filtered and the filtrate was allowed to stand at room temperature during which the white precipitates were formed. The

precipitates were washed with methanol and dried in air. The ligand was used without further purification. *M.p.: 80-82^{o}C, (0.22g, 71 %) Calcd. for $C_{16}H_{18}N_2O_4$: C, 63,58; H, 5.96; N, 9.27%; Found: C, 65.55; H, 5.37; N, 8.81%.*

Synthesis of 3-Ethoxysalicylaldehyde 2-furylbenzoic hydrazone **(L8)**

0.166 g (1.0 mmol) of 3-ethoxysalicylaldehyde in 20 ml methanol was added to a 20 ml hot stirring methanolic solution of 0.126 g (1.0 mmol) of 2-furyl hydrazide. The solution mixture was refluxed for 2 hours. The resulting solution was then filtered and allowed to stand at room temperature during which the white precipitates were formed. The precipitate were washed with methanol and dried in air. The ligand was used without further purification. *M.p.: 95-97^{o}C, (0.25g, 75 %) Calcd. for $C_{14}H_{14}N_2O_4$: C, 61.31; H, 5.11; N, 10.22%; Found: C, 62.10; H, 4.79; N, 10.63%.*

Synthesis of 3-Ethoxysalicylaldehyde salicylhydrazone **(L9)**

0.166 g (1.0 mmol) of 3-ethoxysalicylaldehyde in 20 ml methanol was added to a 20 ml hot stirring methanolic solution of 0.151 g (1.0 mmol) of salicylaldehyde hydrazide. The solution mixture was refluxed for 2 hours. The colourless reaction mixture became cloudy. The resulting solution was then filtered and the filtrate was allowed to stand at room temperature during which the white precipitates were formed. The precipitates were washed with methanol and dried in air. The ligand was used without further purification. *M.p.: 173-175^{o}C, (0.18g, 55 %) Calcd. for $C_{16}H_{16}N_2O_4$: C, 64.00; H, 5.33; N, 9.33%; Found: C, 63.82; H, 5.12; N, 10.02%.*

Synthesis of 3,5-dichlorosalicylaldehyde 2-ethylthiosemicarbazone **(L10)**

0.191 g (1.0 mmol) of 3,5-dichlorosalicylaldehyde in 20 ml methanol was added to a 20 ml hot stirring methanolic solution of 0.119g (1.0 mmol) of 2-ethylthiosemicarbazide. The solution mixture was refluxed for 2 hours. The yellowish reaction mixture became cloudy. The resulting solution was then filtered and the filtrate was allowed to stand at room temperature during which the yellow precipitates were formed. The precipitates were washed with methanol and dried in air. The ligand was used without further purification. *M.p.: 123-125^{o}C, (0.15g, 63 %) Calcd. for $C_{10}H_{12}N_3OSCl_2$: C, 40.96; H, 4.10; N, 16.38; S, 10.92 %; Found: C, 41.07; H, 4.23; N, 16.44; S, 11.21%.*

Synthesis of 3-Ethoxysalicylaldehyde 2,4-dihydroxybenzoic hydrazone **(L11)**

0.166 g (1.0 mmol) of 3-ethoxysalicylaldehyde in 20 ml methanol was added to a 20 ml hot stirring methanolic solution of 0.168g (1.0 mmol) of 2,4-dihydroxybenzoic acid hydrazide. The solution mixture was refluxed for 2 hours. The yellowish reaction mixture became cloudy. The resulting solution was then filtered and the filtrate was allowed to stand at room temperature during which the yellow precipitates were formed. The precipitates were washed with methanol and dried in air. The ligand was used without further purification. *M.p.: 167-169^{o}C, (0.15g, 76 %); Calcd. for $C_{16}H_{16}N_2O_5$: C, 60.56; H, 5.04; N, 8.83; Found: C, 61.08; H, 5.13; N, 9.09%.*

2.4 Preparation of binucleating ligands

General procedures

All the Schiff base ligands **L12** to **L14** were prepared by the condensation reactions of 3-ethoxylsalicylaldehyde, 3,5-dichlorosalicylaldehyde and 4-hydroxysalicylaldehyde with adipic acid dihydrazide in 1:2 ratio, respectively.

Synthesis of 1,4-bis(3-ethoxysalicylaldehyde carbohydrazonato)butane **(L12)**

0.332 g (2.0 mmol) of 3-ethoxysalicylaldehyde in 40 ml ethanol was added to a 30 ml of hot ethanolic solution of 0.174 g (1.0 mmol) of adipic acid dihydrazide. The solution mixture was refluxed with vigorous stirring for 2 hours. The resulting yellow solution was then cooled to room temperature. Upon standing at room temperature for 2 days, the yellow precipitates were filtered and washed with ethanol and dried in air. The ligand was used without further purification. *M.p.: 158-160^{o}C, (0.23 g, 61%) Calcd. for $C_{24}H_{30}N_4O_4$: C, 65.75; H, 6.85; N, 12.76%; Found: C, 66.18; H, 6.70; N, 13.12%.*

Synthesis of 1,4-bis(3,5-dichlorosalicylaldehyde carbohydrazonato)butane **(L13)**

0.382 g (2.0 mmol) of 3,5-dichlorosalicylaldehyde in 40 ml ethanol was added to a 30 ml of hot ethanolic solution of 0.174 g (1.0 mmol) of adipic acid dihydrazide. The solution mixture was refluxed with vigorous stirring for 2 hours. The resulting yellow solution was then cooled to room temperature. Upon standing at room temperature for 2 days, the yellow precipitate was filtered and washed with ethanol and dried in air. The ligand was used without further purification. *M.p.: 240-242^{o}C, (0.22g, 48 %) Calcd. for $C_{20}H_{18}N_4O_4Cl_2$: C, 53.45; H, 4.01; N, 12.47%; Found: C, 53.12; H, 4.09; N, 11.87%.*

***Synthesis of 1,4-bis(4-hydroxysalicylaldehyde carbohydrazonato)butane* (L14)**

0.336 g (2.0 mmol) of 4-hydroxysalicylaldehyde in 40 ml ethanol was added to a 30 ml of hot ethanolic solution of 0.174 g (1.0 mmol) of adipic acid dihydrazide. The solution mixture was refluxed with vigorous stirring for 2 hours. The resulting pale pink solution was then cooled to room temperature. Upon standing at room temperature for 2 days, the white precipitates were filtered and washed with ethanol and dried in air. The ligand was used without further purification. *M.p.: 258-260^{o}C,(0.21g, 34%) Calcd. for $C_{20}H_{22}N_4O_6$: C, 57.97; H, 5.31; N, 13.53%; Found: C, 58.54; H, 5.22; N, 13.27%.*

2.5 Preparation of Mononuclear Dioxomolybdenum (VI) Complexes

The starting complex, bis(acetylacetonato) dioxomolybdenum(VI), [MoO_2 (acac)$_2$] was prepared as described in the literature [46].

Synthesis of [5-Chlorosalicylaldehyde thiosemicarbazonato](dimethylsulfoxide) dioxo-molybdenum (VI) (**C1**)

0.328 g (1.0 mmol) of MoO_2 (acac)$_2$ in 40 ml of methanol was mixed with 40 ml methanol solution containing 0.230 g (1.0 mmol) of 5-chlorosalicylaldehyde thiosemicarbazone. After which, few drops of DMSO were added until the resulting red precipitate dissolved completely. The solution mixture was then refluxed with vigorous stirring for 2 hours. After leaving the solution for 4 days at room temperature, red crystals were formed. The product was filtered and washed with methanol. Single crystals suitable for X-ray diffraction were grown from a mixture of (1:1) of DMSO: MeOH. *M.p.: 208-*

210^{o}C; (0.10g, 22%). Calcd. for $C_{10}H_{12}O_4N_3ClS_2Mo$: C, 37.68; H, 2.77; N, 9.69; S, 14.76%; Found: C, 38.23; H, 3.14; N, 8.31; S, 13.98%.

Synthesis of [5-Chlorosalicylaldehyde 2-ethylthiosemicarbazonato](dimethylsulfoxide) Dioxomolybdenum (VI) **(C2)**

0.328 g (1.0 mmol) of $MoO_2(acac)_2$ in 40 ml of methanol was mixed with 40 ml methanol solution containing 0.258 g (1.0 mmol) of 5-chlorosalicylaldehyde 2-ethylthiosemicarbazone. After which, sufficient amount of DMSO was added until the resulting red precipitates dissolved completely. The solution mixture was then refluxed with vigorous stirring for 2 hours. After leaving the solution for 1 week at room temperature, red crystals were formed. The product was filtered, washed with methanol and dried in air. *M.p.: 208-210^{o}C; (0.10g, 22%) Calcd. for $C_{12}H_{16}O_4N_3ClS_2Mo$: C, 31.17; H, 3.46; N, 9.10; S, 13.85%; Found: C,31.45; H, 3.33; N, 8.89; S, 13.23%.*

General procedures for the preparation of **C3** ***to*** **C15**

A mixture of $MoO_2(acac)_2$ and the ligand in 1:1 ratio in methanol was refluxed. A sufficient amount of dimethylsulfoxide (DMSO), hexamethylphosphoramide (HMPA), dimethylformamide (DMF) or stoichiometric amount of imidazole(Imz) were introduced to the respective solution.

Synthesis of [5-Chlorosalicylaldehyde N-phenylthiosemicarbazonato](dimethylsulfoxide) Dioxomolybdenum (VI) (**C3**)

0.328 g (1.0 mmol) of $MoO_2(acac)_2$ in 40 ml of methanol was mixed with 40 ml methanol solution containing 0.230 g (1.0 mmol) of 5-chlorosalicylaldehyde *N*-phenylthiosemicarbazone. After which, few drops of DMSO were added to the solution.

The solution mixture was then heated to reflux for 2 hours. After leaving the solution for 4 days at room temperature, dark red crystals were formed. The product was filtered, washed with methanol and dried in air. *M.p.: 238-240^{o}C; (0.13g, 25%) Calcd. for $C_{16}H_{16}O_4N_3ClS_2Mo$: C, 37.68; H, 3.14; N, 8.24; S, 12.56%; Found: C,36.78; H, 3.47; N, 8.49; S, 13.02%.*

Synthesis of [3-Ethoxysalicylaldehyde 3-methoxybenzoic hydrazonato](methanol) dioxomolybdenum (VI) **(C4)**

0.328 g (1.0 mmol) of $MoO_2(acac)_2$ in 40 ml of methanol was mixed with 40 ml methanol solution containing 0.302 g (1.0 mmol) of 3-ethoxysalicylaldehyde 3-methoxybenzoic hydrazone . The solution mixture was then refluxed for 2 hours. After leaving the solution for 4 days at room temperature, red crystals were formed. The product was filtered, washed with methanol and dried in *vacuo* over P_4O_{10}. *M.p.: 170-172^{o}C; (0.22g, 43%) Calcd. for $C_{18}H_{20}O_7N_2Mo$: C, 45.76; H, 4.24; N, 5.93%; Found: C, 48.57; H, 4.89; N, 5.33%.*

Synthesis of [3-Ethoxysalicylaldehyde 2-furyl hydrazonato](methanol) dioxo-molybdenum (VI) **(C5)**

0.328 g (1.0 mmol) of $MoO_2(acac)_2$ in 40 ml of methanol was added to a methanolic solution of 0.274 g (1.0 mmol) of 3-ethoxysalicylaldehyde 2-furyl hydrazone. The solution mixture was then refluxed for 2 hours. The resulting red solution on standing in air afforded red crystal. The product was filtered, washed with methanol and dried in *vacuo* over P_4O_{10}. *M.p.: 230-232^{o}C; (0.10g, 23%) Calcd. for $C_{15}H_{16}O_7N_2Mo$: C, 41.67; H, 3.70; N, 6.48%; Found: C, 42.71; H, 3.52; N, 6.49%.*

Synthesis of [5-chlorosalicylaldehyde 3-methoxybenzoic hydrazonato](dimethylsulfoxide) dioxomolybdenum (VI) **(C6)**

0.328 g (1.0 mmol) of $MoO_2(acac)_2$ in 40 ml of methanol was mixed with 40 ml methanol solution of 0.305 g (1.0 mmol) of 5-chlorosalicylaldehyde 3-methoxybenzoic hydrazone. An immediate orange precipitates were formed. A sufficient amount of DMSO was added to the solution until the precipitates were completely dissolved. The solution mixture was then heated to reflux for 2 hours. After leaving the solution for 4 days at room temperature, orange crystals were formed. The product was filtered, washed with methanol and dried in air. *M.p.: 196-198^oC; (0.20g, 32%) Calcd. for $C_{17}H_{17}O_6N_2ClSMo$: C, 40.12; H, 3.34; N, 5.51; S, 6.29%; Found: C, 40.48; H, 3.57; N, 6.63; S, 6.79%.*

Synthesis of [5-chlorosalicylaldehyde 2-furyl hydrazonato](dimethylsulfoxide) dioxomolybdenum (VI) **(C7)**

0.328 g (1.0 mmol) of $MoO_2(acac)_2$ in 40 ml of methanol was mixed with 40 ml methanol solution of 0.253 g (1.0 mmol) of 5-chlorosalicylaldehyde 2-furyl hydrazone. An immediate orange precipitates were formed. A sufficient amount of DMSO was added to the solution until the precipitates were completely dissolved. The solution mixture was then heated to reflux for 2 hours. After leaving the solution for 4 days at room temperature, orange crystals were formed. The product was filtered, washed with methanol and dried in air. *M.p.: 320-322^oC; (0.15g, 19%) Calcd. for $C_{14}H_{13}O_6N_2ClSMo$: C, 35.86; H, 2.77; N, 5.98; S, 6.83%; Found: C, 35.12; H, 2.36; N, 6.25; S, 6.97%.*

Synthesis of [5-chlorosalicylaldehyde 2,4-dihydroxybenzoic hydrazonato](dimethylsulfoxide) dioxomolybdenum (VI) **(C8)**

0.328 g (1.0 mmol) of $MoO_2(acac)_2$ in 40 ml of methanol was mixed with 40 ml methanol solution of 0.308 g (1.0 mmol) of 5-chlorosalicylaldehyde 2,4-dihydroxybenzoic hydrazone. The red solution mixture was then heated to reflux for 1 hour. Then few drops of DMSO were added to the solution and the heating was continued for another 1 hour. The resulting red solution on standing in air afforded red crystals. The product was filtered, washed with methanol and dried in air. *M.p.: 300-302^oC; (0.26g, 34%) Calcd. for $C_{16}H_{15}O_7N_2ClSMo$: C, 37.61; H, 2.94; N, 5.48; S, 6.27%; Found: C, 36.17; H, 3.28; N, 5.55; S, 6.49%.*

Synthesis of [5-chlorosalicylaldehyde 2-furyl hydrazonato](hexamethylphosphoramide) dioxomolybdenum (VI) dimethylformamide solvate **(C9)**

0.328 g (1.0 mmol) of $MoO_2(acac)_2$ in 40 ml of methanol was mixed with 40 ml methanol solution of 0.253 g (1.0 mmol) of 5-chlorosalicylaldehyde 2-furyl hydrazone. An immediate orange precipitation was formed. Few drops of hexamethylphosphoramide were added to the solution. Then a sufficient amount of dimethyformamide was added to the solution until the precipitates were completely dissolved. The solution mixture was then heated to reflux for 2 hours. After leaving the solution for 1 week at room temperature, yellow crystals were formed. The product was filtered, washed with methanol and dried in air. *M.p.: 131-133^oC; (0.17g, 25%) Calcd. for $C_{21}H_{32}O_7N_6ClPMo$: C, 39.34; H, 5.00; N, 13.11%; Found: C, 40.23; H, 4.87; N, 12.68%.*

Synthesis of [3-ethoxysalicylaldehyde 3-methoxybenzoic hydrazonato](dimethylsulfoxide) dioxomolybdenum (VI) **(C10)**

0.328 g (1.0 mmol) of $MoO_2(acac)_2$ in 40 ml of methanol was mixed with 40 ml methanol solution of 0.302 g (1.0 mmol) of 3-ethoxysalicylaldehyde 3-methoxybenzoic hydrazone. The orange solution mixture was then heated to reflux for 1 hour. Then few drops of DMSO were added to the solution and the heating was continued for another 1 hour. The resulting orange solution on standing in air afforded orange coloured crystals. The product was filtered, washed with methanol and dried in air. *M.p.: 184-186^oC; (0.32g, 40%) Calcd. for $C_{19}H_{22}O_7N_2SMo$: C, 44.02; H, 4.52; N, 5.40; S, 6.18%; Found: C, 43.78; H, 4.21; N, 5.25; S, 6.37%.*

Synthesis of [3-ethoxysalicylaldehyde 3-methoxybenzoic hydrazonato] (hexamethyl-phosphoramide) dioxomolybdenum (VI) **(C11)**

0.328 g (1.0 mmol) of $MoO_2(acac)_2$ in 40 ml of methanol was mixed with 40 ml methanol solution of 0.302 g (1.0 mmol) of 3-ethoxysalicylaldehyde 3-methoxybenzoic hydrazone. The orange solution mixture was then heated to reflux for 1 hour. Then few drops of hexamethylphosphoramide were added to the solution and the heating was continued for another 1 hour. The resulting orange solution on standing in air afforded yellow crystals. The product was filtered, washed with methanol and dried in air. *M.p.: 124-126^oC; (0.28g, 37%) Calcd. for $C_{23}H_{34}O_7N_5PMo$: C, 44.59; H, 5.49; N, 11.31%; Found: C, 43.88; H, 4.98; N, 10.73%.*

Synthesis of [3-ethoxysalicylaldehyde 3-methoxybenzoic hydrazonato](dimethylformamide) dioxomolybdenum (VI) **(C12)**

0.328 g (1.0 mmol) of $MoO_2(acac)_2$ in 40 ml of methanol was mixed with 40 ml methanol solution of 0.302 g (1.0 mmol) of 3-ethoxysalicylaldehyde 3-methoxybenzoic hydrazone. The red solution mixture was then heated to reflux for 1 hour. Then few drops of dimethylformamide were added to the solution and the heating was continued for another 1 hour. The resulting red solution on standing in air afforded orange crystals. The product was filtered, washed with methanol and dried in air. *M.p.: 118-120^oC; (0.29g, 41%) Calcd. for $C_{20}H_{22}O_7N_3Mo$: C, 46.88; H, 4.30; N, 8.20%; Found: C, 47.00; H, 4.54; N, 7.77%.*

Syhthesis of [3-ethoxysalicylaldehyde 3-methoxybenzoic hydrazonato](imidazole) dioxo-molybdenum (VI) methanol solvate **(C13)**

0.328 g (1.0 mmol) of $MoO_2(acac)_2$ in 40 ml of methanol was mixed with 40 ml methanol solution of 0.302 g (1.0 mmol) of 3-ethoxysalicylaldehyde 3-methoxybenzoic hydrazone. The orange solution mixture was then heated to reflux for 1 hour. Then 0.070 g of imidazole in 10 ml of methanol was added to the solution and the heating was continued for another 1 hour. The resulting red solution on standing in air afforded red crystals. The product was filtered, washed with methanol and dried in air. *M.p.: 135-137^oC; (0.17g, 42%) Calcd. for $C_{21}H_{26}O_7N_4Mo$: C, 46.49; H, 4.80; N, 10.33%; Found: C, 48.06; H, 4.45; N, 10.89%.*

Synthesis of [3-ethoxysalicylaldehyde 3-methoxybenzoic hydrazonato](tetramethylene sulfoxide) dioxomolybdenum (VI) **(C14)**

0.328 g (1.0 mmol) of $MoO_2(acac)_2$ in 40 ml of methanol was mixed with 40 ml methanol solution of 0.302 g (1.0 mmol) of 3-ethoxysalicylaldehyde 3-methoxybenzoic hydrazone. The orange solution mixture was then heated to reflux for 1 hour. Then few drops of tetramethylene sulfoxide were added to the solution and the heating was continued for another 1 hour. The resulting orange solution on standing in air afforded orange crystals. The product was filtered, washed with methanol and dried in air. *M.p.: 150-152^oC; (0.38g, 46%) Calcd. for $C_{21}H_{24}O_7N_2SMo$: C, 46.32; H, 4.41; N, 5.15; S, 5.88%; Found: C, 46.74; H, 4.96; N, 4.79; S, 6.06%.*

Synthesis of [3-ethoxysalicylaldehyde salicylhydrazonato](dimethyl sulfoxide) dioxomolybdenum (VI) **(C15)**

0.328 g (1.0 mmol) of $MoO_2(acac)_2$ in 40 ml of methanol was mixed with 40 ml methanol solution of 0.300 g (1.0 mmol) of 3-ethoxysalicylaldehyde salicylhydrazone. An immediate red precipitates were formed. A sufficient amount of DMSO was added to the solution until the precipitates were completely dissolved. The solution mixture was then heated to reflux for 2 hours. After leaving the solution for 4 days at room temperature, red crystals were formed. The product was filtered, washed with methanol and dried in air. *M.p.: 170-172^oC; (0.39g, 54%) Calcd. for $C_{18}H_{20}O_7N_2SMo$: C, 42.49; H, 3.97; N, 5.56; S, 6.35%; Found: C, 43.21; H, 4.47; N, 5.69; S, 6.67%.*

2.6 Preparation of 4,4-Bipyridine solvated Dioxomolybdenum (VI) Complexes

***Synthesis of [5-chlorosalicylaldehyde 2,4-dihydroxybenzoic hydrazonato](methanol) dioxomolybdenum(VI) 4,4bipyridine solvate* (C16).**

0.328 g (1.0 mmol) of $MoO_2(acac)_2$ in 40 ml of methanol was mixed with 40 ml methanol solution of 0.308 g (1.0 mmol) of 5-chlorosalicylaldehyde 2,4-dihydroxybenzoic hydrazone. The orange solution mixture was then heated to reflux for 1 hour. Then 0.156 g of 4,4-bipyridine in 10 ml of methanol was added to the solution and the heating was continued for another 1 hour. The resulting orange solution on standing in air afforded orange crystals. The product was filtered, washed with methanol and dried in air. *M.p.: 260-262^oC; (0.32g, 45%) Calcd. for $C_{25}H_{21}O_7N_4ClMo$: C, 48.35; H, 3.38; N, 9.02%; Found: C, 48.14; H, 4.23; N, 8.85%.*

***Synthesis of [3-ethoxysalicylaldehyde 2-furyl hydrazonato] aqua dioxomolybdenum(VI) 4,4bipyridine solvate* (C17)**

0.328 g (1.0 mmol) of $MoO_2(acac)_2$ in 40 ml of methanol was mixed with 40 ml methanol solution of 0.273 g (1.0 mmol) of 3-ethoxysalicylaldehyde 2-furyl hydrazone. The orange solution mixture was then heated to reflux for 1 hour. Then 0.156 g of 4,4-bipyridine in 10 ml of methanol was added to the solution and the heating was continued for another 1 hour. The resulting solution was filtered and the filtrate was allowed to stand at room temperature. Red crystals were formed after slow evaporation for 3 days. The product was filtered, washed with methanol and dried in air. *M.p.: 222-224^oC; (0.37g, 45%) Calcd. for $C_{24}H_{20}O_7N_4Mo$: C, 50.35; H, 3.50; N, 9.79%; Found: C, 49.28; H, 4.33; N, 8.89%.*

2.7 Preparation of Dinuclear Dioxomolybdenum (VI) Complexes

***Synthesis of (μ_2-4,4-Bipyridyl)-bis[(5-chlorosalicylaldehyde 2-ethylthiosemicarbazonato) dioxomolybdenum (VI)]* (C18)**

0.328 g (1.0 mmol) of $MoO_2(acac)_2$ in 40 ml of ethanol was mixed with 40 ml ethanol solution of 0.258 g (1.0 mmol) of 5-chlorosalicylaldehyde 2-ethylthiosemicarbazone. The solution mixture was refluxed with vigorous stirring for 1 hour. Then 0.078 g of 4,4-bipyridine in 10 ml of ethanol solution was added to the mixture and the heating is continued for another 1 hour. After leaving the solution for 1 week at room temperature, dark brown crystals were formed. The product was filtered, washed with ethanol and dried in air. *M.p.: 222-224^oC; (0.25g, 34%) Calcd. for $C_{30}H_{28}O_6N_8S_2Cl_2Mo_2$: C, 39.00; H, 3.03; N, 12.13; S, 6.93%; Found: C, 40.12; H, 3.33; N, 11.67; S, 7.25%.*

***Synthesis of (μ_2-4,4-Bipyridyl N,N'-dioxide)-bis[(3,5-dichlorosalicylaldehyde 2-ethylthio-semicarbazonato) dioxomolybdenum (VI)]* (C19)**

0.328 g (1.0 mmol) of $MoO_2(acac)_2$ in 40 ml of ethanol was mixed with 40 ml ethanol solution of 0.293 g (1.0 mmol) of 3,5-dichlorosalicylaldehyde 2-ethylthiosemicarbazone. The solution mixture was refluxed with vigorous stirring for 1 hour. Then 0.093 g of 4,4-bipyridine N,N'-dioxde in 10 ml of ethanol was added to the mixture and the heating was continued for another 1 hour. After leaving the solution for 1 week at room temperature, dark brown crystals were formed. The product was filtered, washed with ethanol and dried in air. *M.p.: 212-214^oC; (0.32g, 43%) Calcd. for $C_{30}H_{26}O_8N_8S_2Cl_4Mo_2$: C, 35.16; H, 2.54; N, 10.94; S, 6.25%; Found: C, 36.53; H, 2.75; N, 11.11; S, 5.39%.*

Synthesis of 1,4-Bis[(3-ethoxysalicylaldehyde carbohydrazonato)(ethanol) dioxo-molybdenum (VI)]butane **(C20)**

0.656 g (2.0 mmol) of $MoO_2(acac)_2$ in 40 ml of ethanol was mixed with 40 ml ethanol solution of 0.438 g (1.0 mmol) of 1,4-bis(3-ethoxysalicylaldehyde carbohydrazonone) butane. The orange solution mixture was then heated to reflux for 2 hours. After leaving the solution overnight at room temperature, light brown crystals were formed. The product was filtered, washed with ethanol and dried in air. *M.p.: 135-137^oC; (0.47g, 53%) Calcd. for $C_{28}H_{38}O_{12}N_4Mo_2$: C, 41.28; H, 4.67; N, 6.88%; Found: C, 42.36; H, 4.12; N, 7.23%.*

Synthesis of 1,4-Bis[(3,5-dichlorosalicylaldehyde carbohydrazonato) (ethanol) dioxomolybdenum (VI)] butane **(C21)**

0.656 g (2.0 mmol) of $MoO_2(acac)_2$ in 40 ml of ethanol was mixed with 40 ml ethanol solution of 0.438 g (1.0 mmol) of 1,4-bis(3-ethoxysalicylaldehyde carbohydrazonone) butane. The orange solution mixture was then heated to reflux for 2 hours. After leaving the solution for 4 days at room temperature, dark orange crystals were formed. The product was filtered, washed with ethanol and dried in air *M.p.: 310-312^oC; (0.14g, 23%) Calcd. For $C_{24}H_{28}O_{10}N_4Mo_2$: C, 33.26; H, 3.23; N, 6.47%; Found: C, 32.54; H, 3.49; N, 7.29%.*

***Synthesis of 1,4-[Bis(3-ethoxysalicylaldehyde carbohydrazonato (hexamethylphoshoramide) dinuclear dioxomolybdenum (VI)] butane* (C22)**

0.656 g (2.0 mmol) of $MoO_2(acac)_2$ in 40 ml of ethanol was mixed with 40 ml solution of 0.438 g (1.0 mmol) of 1,4-bis(3-ethoxysalicylaldehyde carbohydrazonone) butane. The orange solution mixture was then heated to reflux for 1 hour. Then few drops of hexamethylphosphoramide were added to the solution and an immediate orange precipitates were formed. A sufficient amount of dimethylformamide was added to the mixture until the precipitates completely dissolved. The resulting orange solution was left at room temperature for 5 days during which the yellow solid was formed. Recystallization of the resulting orange solid from dimethylformamide with slow evaporation technique afforded yellow crystals. The product was filtered, washed with ethanol and dried in air. *M.p.: 172-174^oC; (0.37g, 44%) Calcd. for $C_{32}H_{62}O_{12}N_{10}P_2Mo_2$: C, 37.21; H, 6.01; N, 13.57%; Found: C, 36.74; H, 6.42; N, 13.23%.*

***Synthesis of 1,4-Bis[(3-ethoxysalicylaldehyde carbohydrazonato)(dimethylformamide) dioxomolybdenum(VI)]butane* (C23)**

0.656 g (2.0 mmol) of $MoO_2(acac)_2$ in 40 ml ethanol was mixed with 40 ml ethanol solution of 0.438 g (1.0 mmol) of 1,4-bis(3-ethoxysalicylaldehyde carbohydrazonone) butane. The orange solution mixture was then heated to reflux for 1 hour. Then few drops of dimethylformamide was added to the solution and the heating was continued for another 1 hour. After leaving the solution for 1 week at room temperature, yellow crystals were formed. The product was filtered, washed with ethanol and dried in air. *M.p.: 125-127C; (0.29g, 22%) Calcd. for $C_{30}H_{40}O_{12}N_6Mo_2$: C, 41.47; H, 4.61; N, 9.68%; Found: C, 40.88; H, 5.04; N, 10.23%.*

***Synthesis of (μ_2-4,4-Bipyridyl)-bis[1,4-(4-hydroxysalicylaldehyde carbohydrazonato) dioxomolybdenum (VI)]butane-methanol solvate* (C24)**

0.656 g (2.0 mmol) of $MoO_2(acac)_2$ in 40 ml of methanol was mixed with 40 ml methanol solution of 0.414 g (1.0 mmol) of 1,4-bis(4-hydroxysalicylaldehyde carbohydrazonone) butane. The red solution mixture was then heated to reflux for 1 hour. Then 0.078 g of 4,4-bipyridine in 10 ml of methanol was added to the mixture and the heating was continued for another 1 hour. After leaving the solution for 1 week at room temperature, red crystals were formed. The product was filtered, washed with methanol and dried in air. *M.p.: 232-235C; (0.22g, 43%) Calcd. for $C_{15}H_{17}N_3O_5Mo$: C, 43.37; H, 4.09; N, 10.12%; Found: C, 43.88; H, 4.18; N, 10.23%.*

2.8 Catalytic Property of the Oxomolybdenum(VI) Complexes on Oxidation of Benzyl Alcohol

Oxidation of alcohol by dioxomolybdenum(VI) Schiff base complexes with H_2O_2 was carried according to the following procedures. The different reaction condition such as catalyst loading, substrate concentration and reaction temperature were provided to investigate the effect of these factors on catalytic oxidation property of some selective oxomolybdenum(VI) complexes.

2.8.1 Instrumentation

A Shidmazu Model GC 2010 Gas Chromatograph coupled with Shidmazu GC-MS QP 2010 PLUS series mass selective and autosampler was employed for analysis of benzoic acid in the reaction mixture. With the help of autoclavable digital pipette , 10 μL of the reaction mixture diluted by 3 ml of THF was prepared for GC-MS analysis. Samples were separated on 30-m x 0.25 mm, 0.25μm, Rtx-5Ms silica capillary column. The column temperature was initially held at 80^{o}C for 1 minute, then the temperature was raised to 220^{o}C at a rate of 10^{o}C min^{-1}, from 220 to 280^{o}C at a rate of 20^{o}C per minute and hold for 15 minutes. The total run time was 33 minutes. Helium gas was used as carrier gas. Injector temperature was maintained at 300^{o}C and the injection volume was 1.0 μL in the splitless mode. Mass spectra were scanned from m/z 50 – 650 at a rate of 0.5 scan/s. The benzoic acid was identified by matching GC retention time and mass spectra with the standard reference solution.

2.8.2 Preparation of Standard Reference Solution

The standard solution was prepared by dissolving 20-30 mg of benzyl alcohol and benzoic acid in 25 mL of THF.

2.8.3 Screening for Suitable Catalyst for Oxidation of Alcohol after 24 hours

10 cm^3 of benzyl alcohol (10.44 g, 0.1 mol) was mixed with 20 cm^3 of tetrahydrofuran (THF) and 0.5 g (0.001 mol) of the synthesized dioxomolybdenum (VI) complex, **C4,** was added followed by 3 cm^3 of 30% H_2O_2. The mixture was kept under reflux with vigorous stirring at 90^oC for 24 hours. The solution mixture was separated and the THF extracts were evaporated by using rotary evaporator under low pressure before it was treated with Na_2SO_4. The amount of benzoic acid converted was detected by using GCMS. The experiment was repeated by using **C10**, **C11, C12, C13, C14, C16, C17, C18, C19, C20, C21, C22, C23** and **C24** as the catalyst. The benzyl alcohol conversion in the form of percentage was recorded. Blank runs were preformed and as expected, without catalyst, no significant benzoic acid was observed under the applied condition, indicating the catalytic ability of the complexes.

2.8.4 Influence of Catalyst Loading on Oxidation of Alcohol

After determining that **C13**, **C18** and **C24** gave higher catalytic activity to the oxidation of alcohol, the effect of these catalysts concentration was studied.

10 cm^3 of benzyl alcohol (10.44 g, 0.1 mol) was mixed with 20 cm^3 of tetrahydrofuran (THF) and 0.5 g (0.001 mol) of **C13,** was added followed by 3 cm^3 of 30% H_2O_2.. The mixture was kept under reflux with vigorous stirring at 90^oC for 24 hours. 1.0 mL of the solution was taken out, stored in a sample bottle and cooled at 0^oC to terminate the

catalytic oxidation activity. Reflux continued and the solution was taken out for analysis for every 12 hours until 60th hour. The amount of benzoic acid present was detected by using GCMS. The experiments were repeated using 0.002 mol and 0.0025 mol of **C13,** respectively, while the other experimental conditions remained intact. The same procedures were employed to study the effect of the concentration of catalyst on oxidation of alcohol using **C18** and **C24** as catalysts. In each sample, quantification of benzoic acid was conducted by relating the peak areas of identified compound to that of the internal standard. The results of the catalytic performance were recorded.

2.8.5 Influence of Concentration of Substrate

10 cm^3 of benzyl alcohol (10.44 g, 0.1 mol) was mixed with 20 cm^3 of tetrahydrofuran (THF) and 1.08 g (0.002 mol) of the synthesized dioxomolybdenum(VI) complex, **C13,** was added followed by 3 cm^3 of 30% H_2O_2.. The mixture was kept under reflux at 90^{o}C for 24 hours. 1.0 mL of the solution mixture was taken out, stored in a sample bottle and cooled at 0^{o}C to terminate the catalytic oxidation activity. Reflux continued and the solution was taken out for analysis for every 12 hours until the 60th hour. The amount of benzoic acid was detected by using GCMS. The experiments were repeated using 0.2 mol and 0.3 mol of benzyl alcohol**,** respectively, while the other experimental conditions remained intact. Same procedures were employed to study the effect of the concentration of benzyl alcohol as the substrate on oxidation of alcohol using **C24** as catalyst. In each sample, quantification of benzoic acid was conducted by relating the peak areas of identified compound to that of the internal standard. The results of the catalytic performance were recorded.

2.8.6 Influence of Reaction Temperature

10 cm^3 of benzyl alcohol (10.44 g, 0.1 mol) was mixed with 20 cm^3 of tetrahydrofuran (THF) and 1.08 g (0.002 mol) of **C13** was added followed by 3 cm^3 of 30% H_2O_2. The mixture was stirred at room temperature (30^oC) for 24 hours. 1.0 mL of the solution mixture was taken out, stored in a sample bottle and cooled at 0^oC to terminate the catalytic oxidation activity. Stirring was continued and the solution was taken out for analysis for every 12 hours until the 72th hour. The amount of benzoic acid present was detected by using GCMS. The experiments were repeated at 50^oC**,** 70^oC, 90^oC, 110^oC and 130^oC, respectively, while the other experiment conditions remained the same. Similar procedure was employed to study the effect of the reaction temperature on oxidation of alcohol using **C24** as catalyst. In each sample, quantification of benzoic acid was conducted by relating the peak areas of identified compound to that of the internal standard. The results of the catalytic performance were recorded.