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Synthesis, structures, electrochemistry and properties of dioxo-molybdenum(VI) and -tungsten(VI) complexes with novel asymmetric N_2OS, and partially symmetric N_2S_2, NOS_2 *N*-capped tripodal ligands

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Abstract

A new class of asymmetric *N*-capped (dianionic/trianionic) tripodal proligands $[H_x(L^n)]$ ($x = 2$, $n = 1$–6; $x = 3$, $n = 7$, 8) which possess pendant arms with N_2OS, N_2S_2 or NOS_2 donor groups and with different chelate ring sizes {5,5,5} or {5,6,5} has been prepared. Treatment of these ligands with $[WO_2Cl_2(dme)]$ (dme = 1,2-dimethoxyethane) in the presence of base (triethylamine or KOH) leads to the formation of *cis*-dioxotungsten(VI) complexes of the types $[WO_2(L^n)]$ ($n = 1$–6) and $K[WO_2(L^n)]$ ($n = 7$, 8). Reaction of these tetradentate ligands with $[MoO_2(acac)_2]$ (acac = acetylacetonate) gives the corresponding Mo(VI) analogues $[MoO_2(L^n)]$ ($n = 1$–6) and $K[MoO_2(L^n)]$ ($n = 7$, 8). Moreover, a new five coordinate dioxomolybdenum(VI) complex with an NS_2 tridentate ligand $[MoO_2(L^9)]$ has been synthesised using similar procedure. All these compounds have been spectroscopically characterised and the molecular structures of $[MoO_2(L^n)]$ ($n = 2$, 6) and $[WO_2(L^6)]$ have been established by X-ray diffraction analysis. The electrochemistry and the catalytic activity for oxidation of allylic and benzylic alcohols of these dioxo complexes have also been investigated.
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Keywords: Asymmetric tripodal ligands; Dioxomolybdenum(VI) complexes; Dioxotungsten(VI) complexes; Crystal structures; Electrochemistry; Catalytic oxidation

1. Introduction

There has been considerable recent interest in symmetrical *N*-capped tripodal proligands of the type $N[CH_2(CH_2)_nX]_3$ {$n = 1$: X = SH [1], SR [2], NH_2 [3], NHMe, NMe_2 [4], $NH(SiMe_3)$ [5], $NH(C_6F_5)$ [6], OH [7]; $n = 2$: X = NH_2 [8]}. However, the chemistry of asymmetric *N*-capped tripodal ligands which possess three pendant arms with different donor groups has not been well explored [9,10]. This type of ligand is of particular interest in the context of modeling the asymmetric active metal sites such as those found in nitrile hydratase [11], and horse liver alcohol dehydrogenase (HLADH) [12]. We have initially selected the well-known dioxo Mo(VI) and W(VI) cores to explore the coordination chemistry potential of these new ligand systems.

Molybdenum(VI) dioxo-complexes have been extremely thoroughly investigated and there are many literature reports of their syntheses and reactivity, particularly in terms of oxo-transfer reactions [13].

Recently, high-valent oxotungsten complexes have attracted attention owing to their roles in various catalytic processes such as alcohol oxidation [14], olefin epoxidation [15], and olefin metathesis [16]. It is believed

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that most of these organic transformations and biological processes involve oxygen atom transfer (OAT) reactions as one of the crucial steps. Recent studies of tungstoenzymes have stimulated research into the chemistry of tungsten oxo-complexes with sulfur ligands [17], and in particular for those containing dithiolene-type ligands, which provide both structural and functional models for the pterin-containing tungstoenzymes [18]. However, tungsten-mediated oxo-transfer reactions have been rarely studied compared with the related molybdenum chemistry [13] and relatively few examples have been reported [19,20].

We herein report a new series of dioxo-tungsten(VI) and -molybdenum(VI) complexes containing either completely asymmetric (N_2OS with {5,5,5}/{5,6,5} chelate ring-size) or partially symmetric (N_2S_2 or NOS_2) N-capped tripodal ligands, and also a new five coordinate dioxomolybdenum(VI) complex with an NS_2 tridentate ligand; including their synthesis, structures, electrochemistry, and a brief discussion of their catalytic activities for the oxidation of a wide range of allylic and benzylic alcohols without additional peroxide type oxidants.

2. Experimental

2.1. General information

All reactions were carried out using standard Schlenk-line techniques under an atmosphere of dinitrogen; workups were performed in air. Dichloromethane was pre-dried over 4 Å molecular sieves and distilled from calcium hydride. Diethyl ether, tetrahydrofuran (THF) and toluene were distilled from sodium-benzophenone. Methanol (MeOH) was distilled from magnesium methoxide. *N*,*N*-Dimethylformamide (DMF) was dried over barium oxide and distilled under reduced pressure. Silica gel (70-230 mesh) for flash column chromatography was purchased from Fluka. $[MoO_2(acac)_2]$ (acac = acetylacetonate) [21], $[WO_2Cl_2(dme)]$ (dme = 1,2-dimethoxyethane) [22], 2-*N*-(2-pyridylmethyl)aminophenol [23], 2-*N*-(2-pyridylmethyl)amino-4-methylphenol [20d], 2-*N*-(2-pyridylmethyl)amino-4-*tert*-butylphenol [20d], 2-[(2-mercaptoethyl)aminomethyl]pyridine [24], 3,5-di-*tert*-butyl-2-hydroxybenzyl bromide [25], 2-[bis(2-mercaptoethyl)aminomethyl]pyridine (H_2L^6) [26] and *N*,*N*-bis(2-mercaptoethyl)benzylamine (H_2L^9) [27] were prepared according to literature procedures with minor modification. All reagents were used directly as received.

2.2. Instrumentation

All ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Mercury VX300 spectrometer (^1H, 300; ^{13}C, 75.4 MHz). Chemical shifts were relative to internal $SiMe_4$ ($\delta = 0$). IR spectra were recorded on a Perkin–Elmer 1710 spectrophotometer as KBr pellets. Atmospheric pressure chemical ionization (APCI) mass spectra were recorded on a Hewlett-Packard 1050 Series Mass spectrometer. Electrospray ionization (ESI) mass spectra were recorded on a Micromass LCT time-of-flight (TOF) mass spectrometer. Liquid secondary ion (LSI) mass spectra were measured on a Bruker APEX 47e Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with 3-nitrobenzyl alcohol as matrix. Elemental analyses were performed by the microanalysis laboratory of the Inorganic Chemistry Laboratory, University of Oxford, UK. Electrochemical measurements were carried out on a CH Instruments Model 600A electrochemical analyzer. The cell comprised inlets for a platinum-sphere working electrode, a platinum wire counter electrode and a silver wire pseudo-reference electrode. Typically, a 0.1 M solution of $[Bu_4N][BF_4]$ in DMF containing 1.0 mM of sample was purged with nitrogen for 20 min and then the voltammograms were recorded at scan rates ranging from 100 to 2000 mV s^{-1} at ambient temperature. Ferrocene was added as an internal reference and all potentials are reported with respect to the ferrocene/ferrocenium couple at 0.45 V versus SCE [28].

2.3. Synthesis of the ligands

2.3.1. 2-[N-(2-mercaptoethyl)-N-(2-pyridylmethyl)] aminophenol (H_2L^1)

A pale brown suspension of 2-*N*-(2-pyridylmethyl)aminophenol (1.00 g, 5.0 mmol) and ethylene sulfide (0.30 ml, 5.0 mmol) in toluene (5 ml) was heated in a sealed ampoule at 110 °C for 18 h. After cooling to room temperature, the pale brown mixture was loaded onto a silica gel column using $CHCl_3$ followed by $CHCl_3$/ethyl acetate (5:1) as eluant. The second band was collected and concentrated to give a pale yellow liquid. Yield: 0.49 g (38%). ^1H NMR: δ 8.63–8.66 (m, 1H, ArH), 7.66–7.72 (m, 1H, ArH), 7.19–7.27 (m, 2H, ArH), 7.12–7.16 (m, 1H, ArH), 7.02–7.08 (m, 1H, ArH), 6.95–6.99 (m, 1H, ArH), 6.79–6.86 (m, 1H, ArH), 4.12 (s, 2H, $PyCH_2$), 3.24–3.34 (m, 2H, NCH_2CH_2), 2.38–2.48 (m, 2H, NCH_2CH_2). $^{13}C\{^1H\}$ NMR: δ 158.6, 153.6, 148.9, 137.1, 137.0, 125.8, 122.7, 122.5, 119.1, 116.4, 116.1, 61.7, 56.1, 23.3. MS (APCI): *m*/*z* 261 (45%) $[M + H]^+$.

2.3.2. 2-[N-(2-mercaptoethyl)-N-(2-pyridylmethyl)] amino-4-methylphenol (H_2L^2)

This compound was prepared by a procedure analogous to that for H_2L^1. 2-*N*-(2-Pyridylmethyl)amino-4-methylphenol (1.07 g, 5.0 mmol) was treated with ethylene sulfide (0.30 ml, 5.0 mmol) in toluene (5 ml) to give H_2L^2 as a pale yellow liquid. Yield: 0.74 g (54%). ^1H NMR: δ 8.64 (d, $J = 4.2$ Hz, 1H, ArH), 7.67 (t, $J = 7.7$ Hz, 1H, ArH), 7.18–7.25 (m, 2H, ArH), 6.93 (s, 1H,

ArH), 6.82–6.88 (m, 2H, ArH), 4.11 (s, 2H, $PyCH_2$), 3.29 (t, $J = 6.5$ Hz, 2H, NCH_2CH_2), 2.42 (t, $J = 6.5$ Hz, 2H, NCH_2CH_2), 2.26 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR: δ 158.7, 151.1, 148.9, 137.0, 128.3, 126.2, 123.1, 122.6, 122.3, 115.9 (1 peak overlapping), 61.8, 56.3, 23.3, 20.6. MS (APCI): *m/z* 275 (12%) $[M + H]^+$.

2.3.3. 2-[N-(2-mercaptoethyl)-N-(2-pyridylmethyl)] amino-4-tert-butylphenol (H_2L^3)

This compound was prepared by a procedure analogous to that for H_2L^1. 2-*N*-(2-Pyridylmethyl)amino-4-*tert*-butylphenol (1.28 g, 5.0 mmol) was treated with ethylene sulfide (0.30 ml, 5.0 mmol) in toluene (5 ml) to give H_2L^3 as a pale yellow liquid. Yield: 1.07 g (68%). ^1H NMR: δ 8.65 (d, $J = 4.2$ Hz, 1H, ArH), 7.68 (dt, $J = 1.5$, 7.7 Hz, 1H, ArH), 7.19–7.27 (m, 2H, ArH), 7.11 (d, $J = 2.1$ Hz, 1H, ArH), 7.06 (dd, $J = 2.4$, 8.3 Hz, 1H, ArH), 6.90 (d, $J = 8.1$ Hz, 1H, ArH), 4.14 (s, 2H, $PyCH_2$), 3.33 (t, $J = 6.5$ Hz, 2H, NCH_2CH_2), 2.39–2.45 (AB q, 2H, NCH_2CH_2), 1.29 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR: δ 158.8, 151.0, 148.9, 141.9, 137.1, 136.6, 122.7, 122.4, 122.3, 119.5, 115.6, 61.7, 56.1, 34.1, 31.6, 23.3. MS (APCI): *m/z* 317 (100%) $[M + H]^+$.

2.3.4. 2-[N-(3,5-di-tert-butyl-2-hydroxybenzyl)-N-(2-mercaptoethyl)]aminomethyl-pyridine (H_2L^4)

To a colourless mixture of 2-[(2-mercaptoethyl)aminomethyl]pyridine (0.35 g, 2.1 mmol) and triethylamine (0.29 ml, 2.1 mmol) in THF (20 ml) was added chlorotrimethylsilane (0.23 g, 2.1 mmol) dropwise at 0 °C. Some white solid began to form during addition. The mixture was stirred at this temperature for 1 h, then allowed to warm to room temperature. After stirring for 12 h, a second portion of triethylamine (0.29 ml, 2.1 mmol) was added followed by 3,5-di-*tert*-butyl-2-hydroxybenzyl bromide (0.63 g, 2.1 mmol), and the mixture was heated under reflux for 3 h. The mixture was cooled and the resulting white solid was filtered and discarded. The yellow filtrate was concentrated with a rotary evaporator and the residue was chromatographed on a silica gel column using ethyl acetate/hexane (1:2) as eluant. The second band was collected and concentrated to give colourless viscous oil. Yield: 0.63 g (78%). ^1H NMR: δ 8.56 (d, $J = 5.4$ Hz, 1H, PyH), 7.66 (dt, $J = 1.8$, 7.7 Hz, 1H, PyH), 7.34 (d, $J = 7.8$ Hz, 1H, PyH), 7.23 (d, $J = 2.4$ Hz, 1H, ArH), 7.19 (t, $J = 6.2$ Hz, 1H, PyH), 6.86 (d, $J = 2.4$ Hz, 1H, ArH), 3.82 (s, 4H, $PyCH_2$ and $ArCH_2$), 2.83 (t, $J = 7.4$ Hz, 2H, NCH_2CH_2), 2.69 (t, $J = 7.4$ Hz, 2H, NCH_2CH_2), 1.44 (s, 9H, ^{t}Bu), 1.28 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR: δ 157.5, 153.8, 149.1, 140.8, 136.6, 135.8, 123.9, 123.7, 123.2, 122.4, 121.2, 59.4, 59.0, 57.0, 34.9, 34.1, 31.7, 29.6, 21.7. MS (APCI): *m/z* 387 (90%) $[M + H]^+$.

2.3.5. 2-[N-(2-hydroxy-5-nitrobenzyl)-N-(2-mercaptoethyl)]aminomethyl-pyridine (H_2L^5)

This compound was prepared by a procedure analogous to that for H_2L^4 by using 2-hydroxy-5-nitrobenzyl chloride instead of 3,5-di-*tert*-butyl-2-hydroxybenzyl bromide. Yield: 0.60 g (90%). ^1H NMR: δ 8.62 (d, $J = 7.5$ Hz, 1H, ArH), 8.11 (dd, $J = 2.4$, 9.0 Hz, 1H, ArH), 7.99 (d, $J = 3.0$ Hz, 1H, ArH), 7.74 (dt, $J = 1.8$, 7.7 Hz, 1H, Ar*H*), 7.26–7.30 (m, 2H, ArH), 6.93 (d, $J = 9.6$ Hz,, 1H, ArH), 3.94 (s, 2H, $ArCH_2$), 3.82 (s, 2H, $ArCH_2$), 2.82 (t, $J = 7.1$ Hz, 2H, NCH_2CH_2), 2.62 (t, $J = 7.1$ Hz, 2H, NCH_2CH_2). $^{13}C\{^1H\}$ NMR: δ 164.2, 156.6, 148.7, 139.8, 137.3, 125.9, 125.6, 123.1, 122.9, 122.7, 117.1, 58.1, 56.7, 56.3, 22.0. MS (APCI): *m/z* 320 (10%) $[M + H]^+$.

2.3.6. 2-[Bis(2-mercaptoethyl)amino]-3,5-dimethylphenol (H_3L^7)

A dark brown suspension of 6-amino-2,4-dimethylphenol (0.69 g, 5.0 mmol) and ethylene sulfide (0.60 ml, 10.0 mmol) in toluene (10 ml) in a sealed ampoule was heated at 110 °C for 36 h. After cooling to room temperature, the pale brown mixture was loaded onto a silica gel column using CH_2Cl_2 as eluant. The first faint orange band was collected and concentrated to give an orange pungent liquid. Yield: 0.36 g (28%). ^1H NMR: δ 6.77 (d, $J = 2.0$ Hz, 2H, ArH), 3.07 (t, $J = 6.6$ Hz, 4H, NCH_2CH_2), 2.56 (t, $J = 6.6$ Hz, 4H, NCH_2CH_2), 2.23 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR: δ 149.6, 134.3, 129.1, 128.4, 123.7, 120.7, 58.2, 22.9, 20.7, 15.9. MS (APCI): *m/z* 258 (55%) $[M + H]^+$.

2.3.7. 2-[Bis(2-mercaptoethyl)amino]-4-tert-butylphenol (H_3L^8)

This compound was prepared by a procedure analogous to that for H_3L^7. 2-Amino-4-*tert*-butylphenol (1.65 g, 10.0 mmol) was treated with ethylene sulfide (1.2 ml, 20.0 mmol) to give H_3L^8 as an orange pungent liquid. Yield: 0.86 g (30%). ^1H NMR: δ 7.11–7.14 (m, 2H, ArH), 6.88 (d, $J = 9.0$ Hz, 1H, ArH), 3.11 (t, $J = 6.5$ Hz, 4H, NCH_2CH_2), 2.57 (t, $J = 6.5$ Hz, 4H, NCH_2CH_2), 1.27 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR: δ 151.2, 143.2, 134.5, 124.1, 119.9, 114.2, 58.1, 34.3, 31.6, 22.9. MS (APCI): *m/z* 286 (100%) $[M + H]^+$.

2.4. Synthesis of the complexes

2.4.1. [$MoO_2(L^1)$]

To a yellowish-brown solution of H_2L^1 (0.96 g, 3.7 mmol) in MeOH (50 ml) was added $[MoO_2(acac)_2]$ (1.21 g, 3.7 mmol) and the mixture was allowed to stir overnight. The resulting dark brown solid was collected by filtration, washed thoroughly with ethyl acetate, Et_2O and hexane, and then dried in vacuo. Yield: 0.43 g (30%). ^1H NMR (DMSO-d_6): δ 9.00 (d, $J = 3.9$ Hz, 1H, ArH), 7.95 (t, $J = 7.7$ Hz, 1 H, ArH), 7.75 (d,

J = 7.5 Hz, 1H, ArH), 7.57 (t, J = 6.5 Hz, 1 H, ArH), 7.43 (d, J = 8.1 Hz, 1H, ArH), 7.10 (t, J = 8.0 Hz, 1 H, ArH), 6.89 (t, J = 7.5 Hz, 1H, ArH), 6.56 (d, J = 8.4 Hz, 1 H, ArH), 4.76 (d, J = 16.2 Hz, 1H, $PyCH_2$), 4.40–4.51 (m, 2H, $PyCH_2$ and NCH_2CH_2), 3.98–4.07 (m, 1H, NCH_2CH_2), 3.72–3.82 (m, 1H, NCH_2CH_2), 3.58–3.65 (m, 1H, NCH_2CH_2). $^{13}C\{^1H\}$ NMR: δ 160.5, 154.1, 149.1, 140.1, 129.6, 125.1, 124.2, 123.3, 120.4, 117.7 (one peak overlapping), 64.7, 61.9, 31.3. IR (cm^{-1}): 1604m, 1587m, 1542m, 1483s, 1451w, 1420w, 1359w, 1273s, 1157w, 1109w, 1025w, 937s $\nu(MoO_2)$, 901s $\nu(MoO_2)$, 809s, 781s, 756s, 671w, 648w, 631m, 611w, 452w. MS (APCI): m/z 389 (15%) $[M + H]^+$. *Anal.* Calc. for $C_{14}H_{14}MoN_2O_3S$: C, 43.5; H, 3.7; N, 7.3. Found: C, 43.6; H, 3.8; N, 7.3%.

2.4.2. $[MoO_2(L^2)]$

This compound was prepared by a procedure analogous to that for $[MoO_2(L^1)]$. $[MoO_2(acac)_2]$ (0.98 g, 3.0 mmol) was treated with H_2L^2 (0.82 g, 3.0 mmol) in MeOH (30 ml) to give $[MoO_2(L^2)]$ (0.98 g, 82%). ^1H NMR (DMSO-d_6): δ 9.00 (d, J = 3.9 Hz, 1H, ArH), 7.95 (dt, J = 1.8, 7.5 Hz, 1H, ArH), 7.54–7.58 (m, 2H, ArH), 7.44 (d, J = 7.8 Hz, 1H, ArH), 6.91 (dd, J = 1.2, 8.1 Hz, 1H, ArH), 6.45 (d, J = 8.1 Hz, 1H, ArH), 4.73 (d, J = 16.5 Hz, 1H, $PyCH_2$), 4.48 (d, J = 16.5 Hz, 1H, $PyCH_2$), 4.36–4.42 (m, 1H, NCH_2CH_2), 3.96–4.06 (m, 1H, NCH_2CH_2), 3.70–3.79 (m, 1H, NCH_2CH_2), 3.56–3.63 (m, 1H, NCH_2CH_2), 2.25 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR: δ 158.2, 154.1, 149.1, 140.0, 130.1, 129.5, 125.0, 124.1, 123.3, 117.2 (one peak overlapping), 64.6, 61.9, 31.1, 20.4. IR (cm^{-1}): 2922w, 1605w, 1497s, 1458w, 1430w, 1376w, 1276s, 1119w, 1075w, 1053w, 1022w, 925s $\nu(MoO_2)$, 903s $\nu(MoO_2)$, 824m, 813m, 771w, 638w, 611w, 587w, 531w. MS (APCI): m/z 403 (13%) $[M + H]^+$. *Anal.* Calc. for $C_{15}H_{16}MoN_2O_3S$: C, 45.0; H, 4.0; N, 7.0. Found: C, 44.9; H, 4.0; N, 7.0%.

2.4.3. $[MoO_2(L^3)]$

This compound was prepared by a procedure analogous to that for $[MoO_2(L^1)]$. $[MoO_2(acac)_2]$ (0.91 g, 2.8 mmol) was treated with H_2L^3 (0.88 g, 2.8 mmol) in MeOH (30 ml) to give $[MoO_2(L^3)]$ (1.06 g, 86%). ^1H NMR (DMSO-d_6): δ 9.01 (d, J = 3.9 Hz, 1H, ArH), 7.95 (t, J = 7.8 Hz, 1 H, ArH), 7.72 (s, 1H, ArH), 7.56 (t, J = 6.5 Hz, 1H, ArH), 7.44 (d, J = 7.8 Hz, 1H, ArH), 7.12 (d, J = 8.7 Hz, 1H, ArH), 6.47 (d, J = 9.0 Hz, 1H, ArH), 4.74 (d, J = 17.1 Hz, 1H, $PyCH_2$), 4.48–4.55 (m, 2H, $PyCH_2$ and NCH_2CH_2), 3.96–4.05 (m, 1H, NCH_2CH_2), 3.67–3.79 (m, 1H, NCH_2CH_2), 3.56–3.63 (m, 1H, NCH_2CH_2), 1.26 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 158.1, 154.2, 149.1, 143.4, 140.0, 139.7, 126.4, 124.9, 123.4, 120.5, 116.7, 64.6, 62.0, 34.4, 31.5, 31.1. IR (cm^1): 2963m, 2867w, 1604m, 1496s, 1459w, 1441w, 1421m, 1365w, 1287s, 1272s, 1127w, 1075w, 1056w, 1022w, 923s $\nu(MoO_2)$, 903s $\nu(MoO_2)$, 837s, 681w, 647w, 631w, 608w, 541w. MS (APCI): m/z 445 (60%) $[M + H]^+$. *Anal.* Calc. for $C_{18}H_{22}MoN_2O_3S$: C, 48.9; H, 5.0; N, 6.3. Found: C, 48.9; H, 5.4; N, 6.6%.

2.4.4. $[MoO_2(L^4)]$

To a colourless solution of H_2L^4 (0.42 g, 1.1 mmol) in MeOH (30 ml) was added $[MoO_2(acac)_2]$ (0.36 g, 1.1 mmol). After stirring at room temperature for 1.5 h, the resulting mixture was filtered and the volatiles were removed under reduced pressure. The yellow residue was loaded onto a silica gel column using CH_2Cl_2 followed by ethyl acetate as eluant. The intense yellow band was collected and concentrated to give an orange oil, which was triturated with hexane to give an orange yellow solid. Yield: 0.48 g (86%). ^1H NMR (DMSO-d_6): δ 9.03 (d, J = 4.5 Hz, 1H, PyH), 7.78 (dt, J = 1.5, 7.6 Hz, 1H, PyH), 7.38 (t, J = 6.5 Hz, 1H, PyH), 7.14 (d, J = 7.5 Hz, 1H, PyH), 7.10 (d, J = 3.0 Hz, 1H, ArH), 7.04 (d, J = 3.0 Hz, 1H, ArH), 4.86 (d, J = 12.9 Hz, 1H, $ArCH_2$), 4.22 (s, 2H, $ArCH_2$), 4.03–4.15 (m, 2H, $ArCH_2$ and NCH_2CH_2), 3.37–3.53 (m, 2H, NCH_2CH_2), 3.15–3.24 (m, 1H, NCH_2CH_2), 1.22 (s, 9H, ^{t}Bu), 1.17 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR: δ 158.9, 155.9, 150.9, 142.6, 140.1, 137.8, 125.4, 124.2, 124.1, 122.6, 122.5, 66.0, 63.3, 60.1, 35.4, 34.7, 31.9, 30.4, 29.9. IR (cm^{-1}): 2994w, 2951m, 2903w, 2863w, 1605m, 1473m, 1441m, 1424w, 1361w, 1317w, 1300w, 1260m, 1239m, 1205w, 1174w, 1130w, 1022w, 908s $\nu(MoO_2)$, 887s $\nu(MoO_2)$, 849m, 762m, 558m, 479w. MS (APCI): m/z 515 (56%) $[M + H]^+$. *Anal.* Calc. for $C_{23}H_{32}MoN_2O_3S$: C, 53.9; H, 6.3; N, 5.5. Found: C, 53.6; H, 5.9; N, 5.5%.

2.4.5. $[MoO_2(L^5)]$

This compound was prepared by a procedure analogous to that for $[MoO_2(L^1)]$. $[MoO_2(acac)_2]$ (0.65 g, 2.0 mmol) was treated with H_2L^5 (0.64 g, 2.0 mmol) in MeOH (30 ml) to give $[MoO_2(L^5)]$ (0.78 g, 88%). ^1H NMR (DMSO-d_6): δ 8.82 (d, J = 4.2 Hz, 1H, ArH), 8.17 (d, J = 2.7 Hz, 1 H, ArH), 7.74–7.80 (m, 2H, ArH), 7.41 (t, J = 6.5 Hz, 1H, ArH), 7.07 (d, J = 8.1 Hz, 1H, ArH), 6.36 (d, J = 9.3 Hz, 1H, ArH), 4.63 (d, J = 13.5 Hz, 1H, $ArCH_2$), 4.26–4.32 (m, 2 H, $ArCH_2$), 4.02–4.12 (m, 2H, $ArCH_2$ and NCH_2CH_2), 3.46–3.53 (m, 3H, NCH_2CH_2). $^{13}C\{^1H\}$ NMR: δ 167.3, 154.8, 149.3, 140.1, 139.3, 126.4, 125.7, 124.4, 123.9, 122.5, 118.8, 64.2, 60.0, 58.3, 29.4. IR (cm^{-1}): 1607m, 1579w, 1509m $\nu(NO_2)$, 1479m, 1439w, 1421w, 1339s $\nu(NO_2)$, 1289s, 1089m, 917s $\nu(MoO_2)$, 895s $\nu(MoO_2)$, 841w, 800w, 670m. HRMS (LSI): m/z calc. for $C_{15}H_{16}MoN_3O_5S$ $[M + H]^+$ 447.9865, found 447.9867. *Anal.* Calc. for $C_{15}H_{15}MoN_3O_5S$: C, 40.5; H, 3.4; N, 9.4. Found: C, 40.2; H, 3.9; N, 9.1%.

2.4.6. [$MoO_2(L^6)$]

To a colourless solution of H_2L^6 (0.66 g, 2.9 mmol) in MeOH (60 ml) was added [$MoO_2(acac)_2$] (0.95 g, 2.9 mmol). The mixture turned from yellow to orange and then gave a dark brown suspension. After stirring at room temperature for 3 h, the resulting orange-brown solid was collected by filtration, washed thoroughly with MeOH, Et_2O and hexane, and dried in vacuo. Yield: 0.94 g (92%). ^{1}H NMR (DMSO-d_6): δ 8.97 (d, J = 5.1 Hz, 1H, PyH), 8.00 (dt, J = 1.8, 7.7 Hz, 1H, PyH), 7.48–7.53 (m, 2H, PyH), 4.42 (s, 2H, $PyCH_2$), 3.84–3.94 (m, 2H, NCH_2CH_2), 3.46–3.52 (m, 2H, NCH_2CH_2), 3.33–3.40 (m, 2H, NCH_2CH_2), 3.07–3.17 (m, 2H, NCH_2CH_2). $^{13}C\{^1H\}$ NMR: δ 155.4, 149.2, 139.4, 124.3, 121.9, 66.2, 60.0, 32.3. IR (cm^{-1}): 1603m, 1439m, 1297m, 1212w, 1052w, 1019w, 915s ν(MoO_2), 889s ν(MoO_2), 810m, 761w. MS (APCI): *m/z* 357 (50%) $[M + H]^+$. *Anal.* Calc. for $C_{10}H_{14}MoN_2O_2S_2$: C, 33.9; H, 4.0; N, 7.9. Found: C, 34.0; H, 3.7; N, 7.9%.

2.4.7. K[$MoO_2(L^7)$]

A colourless mixture of H_3L^7 (0.26 g, 1.0 mmol) and KOH (0.056 g, 1.0 mmol) in MeOH (100 ml) was added to [$MoO_2(acac)_2$] (0.33 g, 1.0 mmol). The mixture turned deep red immediately. After stirring at room temperature for 1 h, the solution was filtered and the volatiles were removed on a rotary evaporator. The deep red residue was redissolved in acetone (50 ml) and stirred for 15 min. Then the insoluble white solid was filtered and discarded. The filtrate was concentrated to ca. 5 ml and triturated with hexane. The red solid formed was isolated by filtration and then redissolved in ethyl acetate and precipitated with hexane to give a reddish brown solid which was collected by filtration and dried in vacuo. Yield: 0.19 g (46%). ^{1}H NMR (acetone-d_6): δ 6.75 (s, 1H, ArH), 6.63 (s, 1H, ArH), 4.24 (dt, J = 5.1, 11.4 Hz, 2H, NCH_2CH_2), 3.55–3.59 (m, 2H, NCH_2CH_2), 3.02–3.08 (m, 2H, NCH_2CH_2), 2.94 (dt, J = 3.9, 12.3 Hz, 2H, NCH_2CH_2), 2.13 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR: δ 162.2, 135.3, 129.9, 126.2, 123.6, 119.4, 65.9, 31.8, 20.7, 17.5. IR (cm^{-1}): 2926w, 2860w, 1482s, 1309s, 1262m, 902s ν(MoO_2), 873m ν(MoO_2), 819w, 790w, 757w, 641w, 593w. MS (ESI^-): *m/z* 384 (85%) $[M]^-$. *Anal.* Calc. for $C_{12}H_{16}KMoNO_3S_2$: C, 34.2; H, 3.8; N, 3.3. Found: C, 34.6; H, 4.0; N, 3.4%.

2.4.8. K[$MoO_2(L^8)$]

This compound was prepared by a procedure analogous to that for [$MoO_2(L^7)$]. [$MoO_2(acac)_2$] (0.46 g, 1.4 mmol) was treated with H_3L^8 (0.40 g, 1.4 mmol) and KOH (0.079 g, 1.4 mmol) in MeOH (100 ml) to give K[$MoO_2(L^8)$] (0.35 g, 56%). ^{1}H NMR (acetone-d_6): δ 7.14 (d, J = 2.1 Hz, 1H, ArH), 6.96 (dd, J = 2.4, 8.1 Hz, 1H, ArH), 6.53 (d. J = 8.4 Hz, 1H, ArH), 4.25 (dt, J = 5.1, 11.8 Hz, 2H, NCH_2CH_2), 3.65–3.70 (m, 2H, NCH_2CH_2), 3.06–3.11 (m, 2H, NCH_2CH_2), 2.94 (dt, J = 3.9, 12.3 Hz, 2H, NCH_2CH_2), 1.23 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 163.0, 138.7, 135.7, 125.0, 118.3, 117.9, 66.0, 34.6, 32.1, 31.8. IR (cm^{-1}): 2958m, 2861w, 1702w, 1603w, 1498s, 1460w, 1362w, 1307s, 1275m, 1128w, 1077w, 913s ν(MoO_2), 878s ν(MoO_2), 835s, 758m, 671w, 603w, 442w. MS (ESI^-): *m/z* 412 (100%) $[M]^-$. *Anal.* Calc. for $C_{14}H_{20}KMoNO_3S_2$: C, 37.4; H, 4.5; N, 3.1. Found: C, 37.4; H, 5.0; N, 3.0%.

2.4.9. [$MoO_2(L^9)$]

To a warmed solution of [$MoO_2(acac)_2$] (0.98 g, 3.0 mmol) in MeOH (60 ml) at 60 °C was added a colourless solution of H_2L^9 (0.68 g, 3.0 mmol) in MeOH. The mixture turned from yellow to orange and then to a dark brown suspension. After heating for 30 min, the resulting orange-brown solid was collected by filtration, washed thoroughly with MeOH, diethyl ether and hexanes, then dried in vacuo. Yield: 0.72 g (68%). ^{1}H NMR: 7.43–7.45 (m, 3H, ArH), 7.26–7.32 (m, 2H, ArH), 4.65 (s, 2H, $ArCH_2$), 3.85–3.93 (m, 2H, NCH_2CH_2), 3.44–3.57 (m, 4H, NCH_2CH_2), 2.74–2.82 (m, 2H, NCH_2CH_2). $^{13}C\{^1H\}$ NMR: δ 131.9, 130.7, 129.2, 128.9, 58.2, 58.0, 33.3. MS (ESI^+): *m/z* 356 (22%) $[M + H]^+$. IR (cm^{-1}): 934s ν(MoO_2), 903s ν(MoO_2). *Anal.* Calc. for $C_{11}H_{15}MoNO_2S_2$: C, 37.4; H, 4.3; N, 4.0. Found: C, 37.9; H, 4.6; N, 3.8%.

2.4.10. [$WO_2(L^1)$]

To a pale yellow mixture of H_2L^1 (0.39 g, 1.5 mmol) and triethylamine (0.42 ml, 3.0 mmol) in MeOH (30 ml) was added a colourless solution of [WO_2Cl_2(dme)] (0.57 g, 1.5 mmol) in CH_2Cl_2 (20 ml). The mixture turned orange-brown during addition. After stirring for 15 min, some white solid began to form and this mixture was allowed to stir overnight. The white solid formed was collected by filtration, washed with ethanol, ethyl acetate, Et_2O and hexane, and dried in vacuo. Yield: 0.38 g (53%). ^{1}H NMR (DMSO-d_6): δ 9.07 (d, J = 5.4 Hz, 1H, ArH), 8.02 (t, J = 7.5 Hz, 1H, ArH), 7.78 (d, J = 8.4 Hz, 1H, ArH), 7.61 (t, J = 6.2 Hz, 1H, ArH), 7.51 (d, J = 8.1 Hz, 1H, ArH), 7.15 (t, J = 7.1 Hz, 1H, ArH), 6.94 (t, J = 7.7 Hz, 1H, ArH), 6.61 (d, J = 8.1 Hz, 1H, ArH), 4.72–4.87 (AB q, 2H, $PyCH_2$), 4.55–4.60 (m, 1H, NCH_2CH_2), 3.84–3.96 (m, 2H, NCH_2CH_2), 3.58–3.64 (m, 1H, NCH_2CH_2). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 159.6, 155.0, 149.4, 140.5, 139.9, 129.9, 125.1, 124.3, 123.6, 121.0, 118.8, 65.2, 61.4, 29.6. IR (cm^{-1}): 1607m, 1589m, 1484s, 1451m, 1420m, 1306w, 1273s, 1253m, 1233w, 1159w, 1108w, 1058w, 1028w, 948s ν(WO_2), 907s ν(WO_2), 859w, 825w, 781m, 757m, 649w, 637m. MS (APCI): *m/z* 475 (10%) $[M + H]^+$. *Anal.* Calc. for $C_{14}H_{14}N_2O_3SW$: C, 35.5; H, 3.0; N, 5.9. Found: C, 35.6; H, 3.1; N, 6.0%.

2.4.11. [$WO_2(L^2)$]

This compound was prepared by a procedure analogous to that for [$WO_2(L^1)$]. [WO_2Cl_2(dme)] (0.87 g, 2.3 mmol) was treated with H_2L^2 (0.63 g, 2.3 mmol) and triethylamine (0.64 ml, 4.6 mmol) in MeOH (20 ml)/CH_2Cl_2 (20 ml) to give [$WO_2(L^2)$] (0.68 g, 61%). ^{1}H NMR (DMSO-d_6): δ 9.06 (d, J = 5.1 Hz, 1H, ArH), 8.01 (t, J = 7.7 Hz, 1H, ArH), 7.59–7.62 (m, 2H, ArH), 7.51 (d, J = 8.1 Hz, 1H, ArH), 6.96 (d, J = 8.1 Hz, 1H, ArH), 6.50 (d, J = 8.1 Hz, 1H, ArH), 4.72–4.85 (AB q, 2H, $PyCH_2$), 4.52–4.56 (m, 1H, NCH_2CH_2), 3.79–3.97 (m, 2H, NCH_2CH_2), 3.56–3.62 (m, 1H, NCH_2CH_2), 2.26 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 157.2, 155.0, 149.4, 140.4, 139.5, 130.4, 130.1, 125.1, 124.2, 123.6, 118.2, 65.0, 61.4, 29.5, 20.4. IR (cm^{-1}): 2924w, 1607m, 1499s, 1458w, 1431m, 1377w, 1276s, 1153w, 1117w, 1054w, 1025w, 949s $\nu(WO_2)$, 909s $\nu(WO_2)$, 827m, 813m, 772w, 641w, 533w. MS (APCI): *m/z* 489 (20%) $[M + H]^+$. *Anal.* Calc. for $C_{15}H_{16}N_2O_3SW$: C, 36.9; H, 3.3; N, 5.7. Found: C, 36.6; H, 3.4; N, 5.9%.

2.4.12. [$WO_2(L^3)$]

This compound was prepared by a procedure analogous to that for [$WO_2(L^1)$]. [WO_2Cl_2(dme)] (0.75 g, 2.0 mmol) was treated with H_2L^3 (0.63 g, 2.0 mmol) and triethylamine (0.55 ml, 4.0 mmol) in MeOH (30 ml)/CH_2Cl_2 (20ml) to give [$WO_2(L^3)$] (0.84 g, 79%). ^{1}H NMR (DMSO-d_6): 9.07 (d, J = 4.8 Hz, 1H, ArH), 8.02 (t, J = 7.7 Hz, 1H, ArH), 7.74 (d, J = 2.4 Hz, 1H, ArH), 7.60 (t, J = 6.5 Hz, 1H, ArH), 7.52 (d, J = 7.8 Hz, 1H, ArH), 7.17 (dd, J = 1.8, 8.7 Hz, 1H, ArH), 6.52 (d, J = 8.4 Hz, 1H, ArH), 4.73–4.86 (AB q, 2H, $PyCH_2$), 4.64–4.69 (m, 1H, NCH_2CH_2), 3.79–3.93 (m, 2H, NCH_2CH_2), 3.56–3.62 (m, 1H, NCH_2CH_2), 1.26 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 157.1, 155.2, 149.4, 144.0, 140.5, 139.4, 126.7, 125.0, 123.6, 120.6, 117.8, 65.1, 61.5, 34.4, 31.5, 29.5. IR (cm^1): 2959m, 2904w, 2869w, 1607m, 1498s, 1425m, 1363w, 1278s, 1233w, 1127w, 1056w, 1024w, 949s $\nu(WO_2)$, 909s $\nu(WO_2)$, 837s, 820m, 788w, 769w, 682w, 649w, 633w. MS (APCI): *m/z* 531 (35%) $[M + H]^+$. *Anal.* Calc. for $C_{18}H_{22}N_2O_3SW$: C, 40.8; H, 4.2; N, 5.3. Found: C, 40.7; H, 4.6; N, 5.3%.

2.4.13. [$WO_2(L^4)$]

To a colourless mixture of H_2L^4 (0.89 g, 2.3 mmol) and triethylamine (0.64 ml, 4.6 mmol) in CH_2Cl_2 (20 ml) was added a solution of [WO_2Cl_2(dme)] (0.87 g, 2.3 mmol) in CH_2Cl_2 (30 ml). The mixture turned dark brown immediately. After stirring overnight, the volatiles were removed under reduced pressure and the residue was transferred to a silica gel column using CH_2Cl_2 first followed by ethyl acetate as eluant. The second band was collected and concentrated to give a pale yellow oil which was then triturated with hexane to give a pale yellow solid. Yield: 0.59 g (43%). ^{1}H NMR: δ 9.20 (d, J = 4.8 Hz, 1H, PyH), 7.66 (dt, J = 1.8, 7.8 Hz, 1H, PyH), 7.26 (t, J = 6.5 Hz, 1H, PyH), 7.09 (d, J = 2.4 Hz, 1H, ArH), 6.89–6.94 (m, 2H, PyH and ArH), 5.05 (d, J = 12.9 Hz, 1H, $ArCH_2$), 4.28 (d, J = 16.2 Hz, 1H, $ArCH_2$), 4.10–4.19 (m, 2H, $ArCH_2$ and NCH_2CH_2), 3.81 (d, J = 12.9 Hz, 1H, $ArCH_2$), 3.60–3.67 (m, 1H, NCH_2CH_2), 3.50–3.57 (m, 1H, NCH_2CH_2), 3.20–3.29 (m, 1H, NCH_2CH_2), 1.22 (s, 9H, ^{t}Bu), 1.18 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR: δ 156.1, 154.9, 151.1, 142.9, 139.3, 138.4, 124.4, 124.0, 123.5, 121.1, 120.8, 66.0, 63.3, 60.4, 34.8, 34.2, 31.6, 30.0, 28.2. IR (cm^{-1}): 2956s, 2868m, 1608m, 1476s, 1443s, 1361w, 1304w, 1261s, 1240s, 1208w, 1171w, 943s $\nu(WO_2)$, 900s $\nu(WO_2)$, 849s, 759m, 559m. MS (APCI): *m/z* 601 (95%) $[M + H]^+$. *Anal.* Calc. for $C_{23}H_{32}N_2O_3SW$: C, 46.0; H, 5.4; N, 4.7. Found: C, 46.7; H, 6.2; N, 4.4%.

2.4.14. [$WO_2(L^5)$]

This compound was prepared by a procedure analogous to that for [$WO_2(L^1)$]. [WO_2Cl_2(dme)] (0.75 g, 2.0 mmol) was treated with H_2L^5 (0.64 g, 2.0 mmol) and triethylamine (0.55 ml, 4.0 mmol) in MeOH (20 ml)/CH_2Cl_2 (20 ml) to give [$WO_2(L^5)$] (0.83 g, 78%). ^{1}H NMR (DMSO-d_6): 8.88 (d, J = 4.5 Hz, 1H, ArH), 8.19 (d, J = 3.0 Hz, 1H, ArH), 7.81–7.86 (m, 2H, ArH), 7.46 (t, J = 6.5 Hz, 1H, ArH), 7.15 (d, J = 7.5 Hz, 1H, ArH), 6.44 (d, J = 8.7 Hz, 1H, ArH), 4.66 (d, J = 13.5 Hz, 1H, $ArCH_2$), 4.24–4.42 (m, 3H, $ArCH_2$), 3.95–4.05 (m, 1H, NCH_2CH_2), 3.64–3.68 (m, 1H, NCH_2CH_2), 3.54–3.56 (m, 2H, NCH_2CH_2). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 165.7, 155.7, 149.6, 140.6, 139.9, 126.3, 125.8, 124.6, 124.1, 122.6, 119.1, 64.5, 59.9, 58.8, 27.6. IR (cm^{-1}): 1609m, 1581w, 1513m $\nu(NO_2)$, 1481m, 1440w, 1422w, 1341s $\nu(NO_2)$, 1285s, 1088m, 942s $\nu(WO_2)$, 900s $\nu(WO_2)$, 842w, 801w, 673w. HRMS (LSI): *m/z* calc. for $C_{15}H_{16}N_3O_5SW$ $[M + H]^+$ 534.0320, found 534.0303. *Anal.* Calc. for $C_{15}H_{15}N_3O_5SW$: C, 33.8; H, 2.8; N, 7.9. Found: C, 33.5; H, 3.5; N, 7.6%.

2.4.15. [$WO_2(L^6)$]

A colourless solution of H_2L^6 (0.57 g, 2.5 mmol) in MeOH (20 ml) was added triethylamine (0.69 ml, 5.0 mmol) with vigorous stirring. After stirring at room temp for 15 min, a colourless solution of [WO_2Cl_2(dme)] (0.94 g, 2.5 mmol) in CH_2Cl_2 (30 ml) was added dropwise *via* a cannula to this solution. The mixture turned cloudy immediately and some pale yellow solid began to form. This mixture was allowed to stir for 5 h. Then the pale yellow solid formed was isolated by filtration, washed thoroughly with MeOH, ethyl acetate, Et_2O and hexane, and dried in vacuo. Yield: 0.62 g (56%). ^{1}H NMR (DMSO-d_6): δ 9.00 (dd, J = 1.2, 5.9 Hz, 1H, PyH), 8.06 (dt, J = 1.8, 7.7 Hz, 1H, PyH), 7.52–7.56 (m, 2H, PyH), 4.58 (s, 2H, $PyCH_2$), 3.74–3.82 (m, 2H,

NCH_2CH_2), 3.61–3.67 (m, 2H, NCH_2CH_2), 3.51–3.57 (m, 2H, NCH_2CH_2), 3.12–3.22 (m, 2H, NCH_2CH_2). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 156.5, 149.4, 139.8, 124.5, 122.1, 66.1, 60.5, 31.2. IR (cm^1): 2955w, 2862w, 1605m, 1482w, 1457w, 1439w, 1422w, 1298m, 1213w, 1083w, 1052w, 945s $\nu(WO_2)$, 897s $\nu(WO_2)$, 839w, 795w, 763m. MS (APCI): *m/z* 443 (58%) $[M + H]^+$. *Anal.* Calc. for $C_{10}H_{14}N_2O_2S_2W$: C, 27.2; H, 3.2; N, 6.3. Found: C, 27.3; H, 3.4; N, 6.2%.

2.4.16. $K[WO_2(L^7)]$

A colourless mixture of H_3L^7 (0.23 g, 0.9 mmol) and KOH (0.15 g, 2.6 mmol) in MeOH (60 ml) was added to $[WO_2Cl_2(dme)]$ (0.34 g, 0.9 mmol). The mixture turned dark purple immediately. After stirring at room temperature for 12 h, the solution was filtered before being concentrated using rotary evaporator. The dark purple residue was redissolved in acetone (50 ml) and stirred for 15 min. The insoluble white solid was filtered and discarded. The filtrate was concentrated to ca. 5 ml and triturated with hexane to give a reddish solid which was isolated by filtration, washed thoroughly with ethyl acetate and acetone/hexane (1:3) to give a pale yellow solid. Yield: 0.16 g (36%). ^1H NMR (acetone-d_6): δ 6.76 (s, 1H, ArH), 6.68 (s, 1H, ArH), 4.21 (dt, $J = 4.8$, 11.7 Hz, 2H, NCH_2CH_2), 3.68 (dd, $J = 4.2$, 10.1 Hz, 2H, NCH_2CH_2), 3.23 (dd, $J = 4.8$, 11.7 Hz, 2H, NCH_2CH_2), 2.94 (dt, $J = 4.5$, 12.5 Hz, 2H, NCH_2CH_2), 2.15 (s, 3H, CH_3), 2.12 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 162.1, 135.4, 130.4, 127.4, 124.8, 119.8, 65.7, 31.1, 20.6, 17.2. IR (cm^{-1}): 2925w, 2858w, 1485s, 1459m, 1310s, 1261m, 1211w, 1075w, 981w, 927s $\nu(WO_2)$, 876s $\nu(WO_2)$, 819m, 791w, 757w, 677w, 645w, 595w, 499w, 453m. MS (ESI^-): *m/z* 470 (100%) $[M]^-$. *Anal.* Calc. for $C_{12}H_{16}KNO_3S_2W$: C, 28.3; H, 3.2; N, 2.8. Found: C, 28.6; H, 3.5; N, 3.0%.

2.4.17. $K[WO_2(L^8)]$

This compound was prepared according to the procedure analogous to that for $K[WO_2(L^7)]$. $[WO_2Cl_2(dme)]$ (0.41 g, 1.1 mmol) was treated with H_3L^8 (0.31 g, 1.1 mmol) and KOH (0.19 g, 3.4 mmol) in MeOH (60 ml) to give $K[WO_2(L^8)]$ (0.22 g, 38%). ^1H NMR (acetone-d_6): δ 7.15 (d, $J = 2.4$ Hz, 1H, ArH), 7.01 (dd, $J = 2.4$, 8.1 Hz, 1H, ArH), 6.51 (d. $J = 8.7$ Hz, 1H, ArH), 4.21 (dt, $J = 4.8$, 12.1 Hz, 2H, NCH_2CH_2), 3.79 (dd, $J = 4.8$, 10.2 Hz, 2H, NCH_2CH_2), 3.26 (dd, $J = 4.8$, 11.4 Hz, 2H, NCH_2CH_2), 2.93 (dt, $J = 4.8$, 12.5 Hz, 2H, NCH_2CH_2), 1.24 (s, 9H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 163.2, 139.4, 135.9, 125.5, 119.0, 118.7, 65.7, 34.6, 32.1, 31.1. IR (cm^{-1}): 2960m, 2864w, 1499s, 1459w, 1363w, 1307s, 1277w, 1128w, 1076w, 927s $\nu(WO_2)$, 877s $\nu(WO_2)$, 835m, 759m, 671w, 607w, 451w. MS (ESI^-): *m/z* 498 (100%) $[M]^-$. *Anal.* Calc. for $C_{14}H_{20}KNO_3S_2W$: C, 31.3; H, 3.8; N, 2.6. Found: C, 31.5; H, 4.0; N, 2.8%.

2.5. General procedure for screening the catalytic activity of the complexes towards alcohol oxidation under anaerobic condition

A mixture of metal complex $\{[MO_2(L^n)]$ (M = Mo, W; $n = 3-6$, 8, 9)$\}$ (5 mol%) and benzoin (0.2 mmol) in DMSO-d_6 (0.5 ml) was placed in a NMR tube equipped with Young's Teflon tap. The mixture was degassed and heated at 100 °C. The catalytic product (benzil) was identified by comparing the ^1H NMR spectrum with that of the authentic sample. The percentage conversion of the product was determined by ^1H NMR spectroscopy.

2.6. General procedure for the alcohol oxidation catalysed by $[MoO_2(L^9)]$ under aerobic condition

A mixture of substrate (0.2 mmol) and $[MoO_2(L^9)]$ (5 mol%) in DMSO-d_6 (0.5 ml) was placed in a 10 ml round bottom flask equipped with a water condenser. The mixture was heated at 100 °C in air. The catalytic product was identified by comparing the ^1H NMR spectrum with that of the authentic sample. The percentage conversion of the products was determined by ^1H NMR spectroscopy.

2.7. X-ray crystal structure determination of $[MoO_2(L^2)]$, $[MoO_2(L^6)]$ and $[WO_2(L^6)]$

Single crystals of $[MoO_2(L^2)]$ and $[MoO_2(L^6)]$ suitable for X-ray diffraction were grown from DMF by slow evaporation. A suitable crystal of $[WO_2(L^6)]$ was obtained by slow cooling of a warm solution in DMSO-d_6 in an NMR tube. Crystal data and data processing parameters are given in Table 3. Crystals were mounted on a glass fiber using perfluoropolyether oil and cooled rapidly to 150K in a stream of cold nitrogen using an Oxford Cryosystems CRYOSTREAM unit. For $[MoO_2(L^2)]$ and $[WO_2(L^6)]$, diffraction data were collected on an Enraf-Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å). Intensity data were processed using the DENZO-SMN package [29]. For $[MoO_2(L^6)]$, diffraction data were collected on an Enraf-Nonius DIP2000 image-plate diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.71069$ Å). Ninety frames of data were collected (2° oscillation per frame, 900 s exposure). Intensity data were processed using the programs DENZO and SCALEPACK [29]. All these structures were solved using the direct-methods program SIR92 [30], which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite [31]. Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were positioned geometrically after each cycle of refinement. 4-Term {for $[MoO_2(L^2)]$}, 3-term {for

[$MoO_2(L^6)$]} and 5-term {for [$WO_2(L^6)$]} Chebychev polynomial weighting schemes were applied.

3. Results and discussion

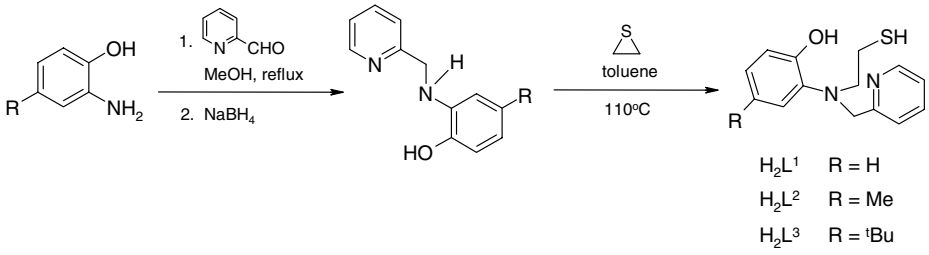
3.1. Synthesis and spectroscopic characterisation

The asymmetric N_2OS *N*-capped tripodal proligands H_2L^n (n = 1–3) were prepared by a reaction involving two steps (Scheme 1). Reductive amination of 2-pyridinecarboxaldehyde and the respective 2-aminophenol gave the corresponding substituted 2-*N*-(2-pyridylmethyl)aminophenol [23]. Further reaction of these N_2O precursors with 1 equivalent of ethylene sulfide in a sealed ampoule gave the new asymmetric N_2OS tripodal proligands with {5,5,5} chelate ring systems in 38–68% yield. Interestingly, the reaction yield increased with the size of the alkyl chain (methyl or *tert*-butyl) on the phenolic ring, probably due to the improved solubility of N_2O precursors, which enhanced the reaction with ethylene sulfide. We have also tried to extend the above synthetic pathway to prepare proligands with {5,6,5} chelate ring systems. However, attempts to synthesise H_2L^n (n = 4, 5) by the reaction of 2-*N*-(3,5-di-*tert*-butyl-2-hydroxybenzyl)aminomethylpyridine [20a] or 2-*N*-(2-hydroxy-5-nitrobenzyl)aminomethylpyridine [32] with 1 equivalent of ethylene sulfide using identical conditions as for those of H_2L^n (n = 1–3) was not successful. After workup procedure, only the N_2O precursors were regenerated. The white insoluble material formed in the reaction mixture suggested that self-polymerization of ethylene sulfide occurred rather than *N*-alkylation.

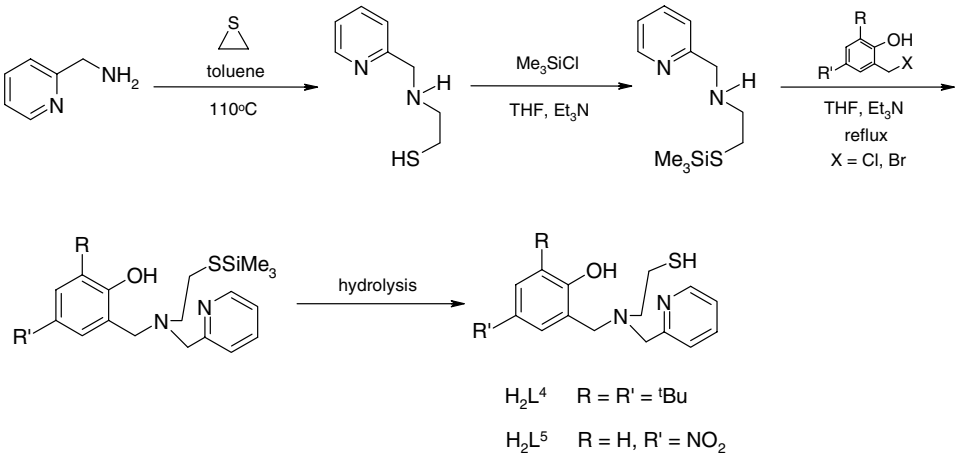
A modified strategy for the synthesis of H_2L^n (n = 4, 5) is shown in Scheme 2. These proligands were synthesised by a reaction involving four steps, three of which were performed in situ. The first step was based on a literature procedure with minor modification [24]. Reaction of 2-aminomethylpyridine with 1 equivalent of ethylene sulfide gave 2-[(2-mercaptoethyl)aminomethyl]pyridine in 68% yield. This compound was purified by flash column chromatography rather than vacuum distillation in order to prevent the possibility of regenerating the starting materials by decomposition during prolonged heating. Treatment of this N_2S precursor with chlorotrimethylsilane in the presence of triethylamine gave the silyl thioether adduct which was then *N*-alkylated with a variety of substituted 2-hydroxybenzyl bromides to afford the silyl-protected N_2OS proligands. Hydrolysis of these potential ligands during workup and purifying procedures led to the formation of new N_2OS tetradentate proligands H_2L^n (n = 4, 5) in 78–90% yield. Although silyl reagents have been conventionally used as protecting groups for alcohols and amines, they are seldom used for thiol protection, mainly due to the instability of the silyl thioether type compounds in protic media [33]. By employing this synthetic scheme with the silyl reagent, we were able to extend the range of asymmetric N_2OS ligands H_2L^n (n = 1–3) from those {5,5,5} chelate ring systems to those with {5,6,5}. The versatility of this synthetic route using silyl reagent has also recently been demonstrated by the preparation of a new class of N_2S tridentate ligands [34].

Due to the flexibility and length of the pendant arms, the proligands H_2L^n (n = 1–5) are capable of providing a N_2OS coordination environment for a metal without any steric hindrance, and may generate a chiral mononuclear complex upon coordination. Apart from the strongly asymmetric systems, partially symmetric tripodal tetradentate proligands H_xL^n [x = 2, n = 6 (N_2S_2); x = 3, n = 7, 8 (NOS_2)] and a NS_2 tridentate proligand H_2L^9 have also been prepared (Schemes 3–5). The N_2S_2 proligand was first reported by reaction of 2-aminomethylpyridine with 2 equivalents of ethylene sulfide to give H_2L^6 in 72% yield. This proligand was again purified by flash column chromatography rather than vacuum distillation due to the reason stated above. The trivalent NOS_2 proligands H_2L^n (n = 7, 8) and divalent NS_2 proligand H_2L^9 were prepared using similar procedure as for H_2L^6. All these sulfur-containing proligands H_xL^n (x = 2, n = 1–6, 9; x = 3, n = 7, 8) are very sensitive to air and easily oxidise to give the disulfide. Therefore they must be stored under a dinitrogen atmosphere at low temperature (−30 °C) prior to use.

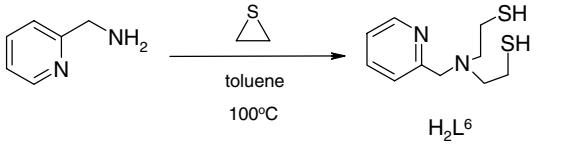
In the preparation of dioxotungsten(VI) complexes, [WO_2Cl_2(dme)] (dme = 1,2-dimethoxyethane) was employed as starting material [22]. This dme adduct is extremely soluble in common organic solvents such as



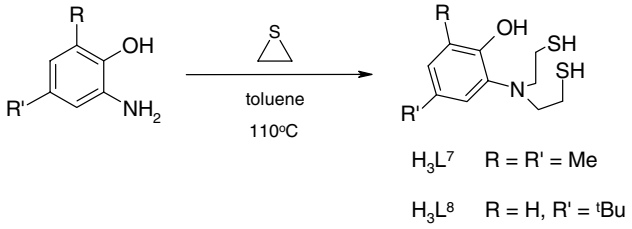
Scheme 1.



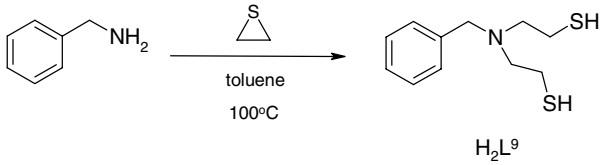
Scheme 2.



Scheme 3.



Scheme 4.

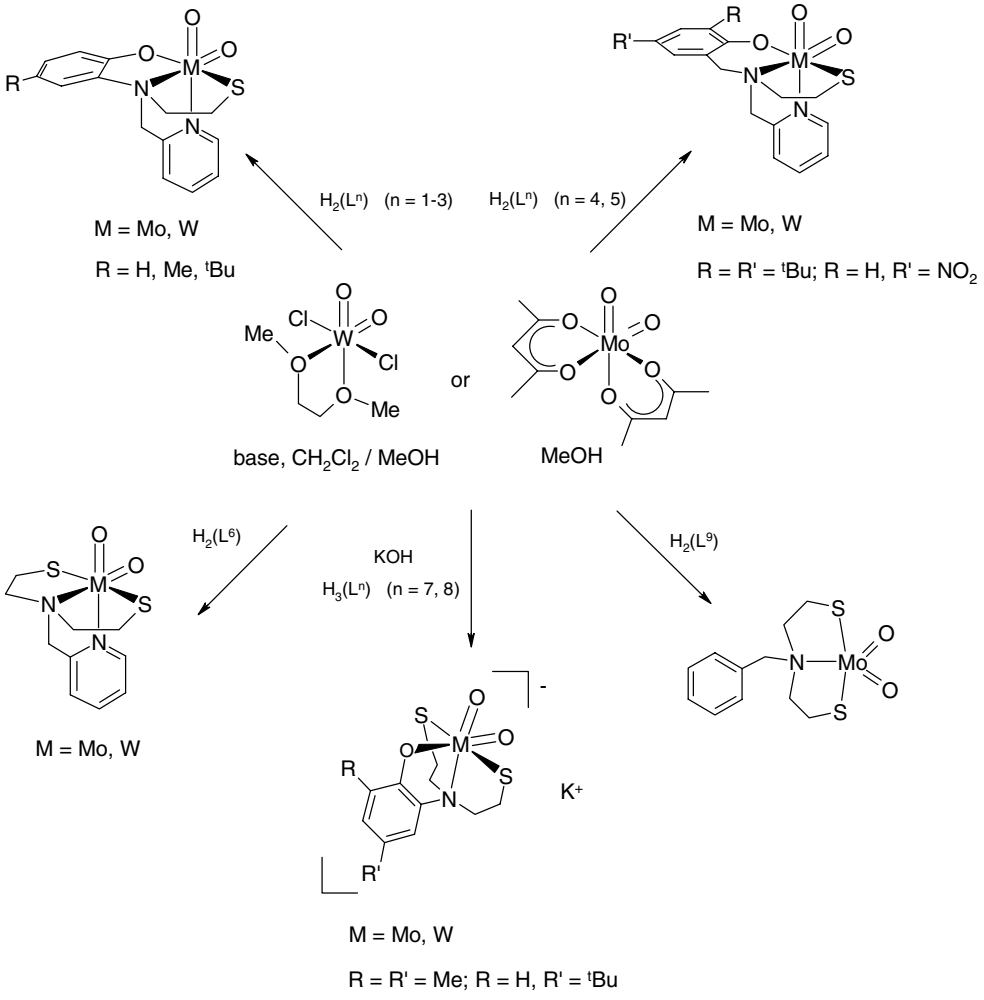


Scheme 5.

THF, CH_2Cl_2 and acetonitrile which is in contrast to the conventionally used reagents such as $[WO_2(acac)_2]$ (acac = acetylacetonate) [35] and $[WO_2Cl_2]$ [35c,36]. Moreover, this dme reagent is highly reactive towards a wide range of ligand substitution reactions [20,23,34,37]. Treatment of the proligands H_xL^n ($x = 2$, $n = 1$–6; $x = 3$, $n = 7$, 8) with $[WO_2Cl_2(dme)]$ in the presence of base (triethylamine or KOH) gave the corresponding dioxo compounds $[WO_2(L^n)]$ ($n = 1$–6) and $K[WO_2(L^n)]$ ($n = 7$, 8) in moderate to good yield (Scheme 6). All these dioxotungsten(VI) compounds are stable to air and moisture, and white in colour except for $[WO_2(L^6)]$ and $K[WO_2(L^n)]$ ($n = 7$, 8) which are pale yellow.

The molybdenum analogues were also prepared for comparison. Treatment of $[MoO_2(acac)_2]$ (acac = acetylacetonate) with the proligands H_xL^n ($x = 2$, $n = 1$–6, 9; $x = 3$, $n = 7$, 8) in MeOH (KOH was added in the case of potentially trianionic ligands to provide potassium as source of counter ion) gave the dioxo complexes (Scheme 6). All these dioxomolybdenum(VI) compounds are stable to air and moisture, and orange in colour except for $[MoO_2(L^n)]$ ($n = 1$–3) which are yellow. Due to the limited solubility of most of these dioxo–tungsten(VI) and –molybdenum(VI) complexes, the crude products were collected by filtration, washed with organic solvents followed by recrystallisation. This procedure was used for the complexes $[MO_2(L^n)]$ (M = Mo, W; $n = 1$–3, 5, 6, 9) and $K[MO_2(L^n)]$ (M = Mo, W; $n = 7$, 8); whereas $[MO_2(L^4)]$ (M = Mo, W) containing two *tert*-butyl groups on the ligand possess sufficient solubility to be purified by column chromatography.

All these complexes have appropriate microanalyses. The infra-red spectra show two strong bands in the regions 873–909 and 902949 cm^{-1} which are attributable to the asymmetric and symmetric M = O (M = Mo, W) stretches respectively in a *cis*-dioxo moiety [38,39]. The spectra of compounds containing nitro groups also displayed strong bands at 1339–1341 and 1509–1513 cm^{-1} which arise from the stretching vibrations of the C–NO_2 unit [40]. The ^1H and $^{13}C\{^1H\}$ NMR data for these complexes are consistent with the proposed octahedral structures. For complexes with asymmetric ligands $[MO_2(L^n)]$ (M = Mo, W; $n = 1$–3), the appearance of two doublets at δ 4.40–4.72 and 4.73–4.87 for the two methylene protons adjacent to the pyridine ring in the ^1H NMR spectra shows that two methylene protons



Scheme 6.

become diastereotopic after complexation. All dioxo complexes have been characterised by the detection of the $[M + 1]^+$ ions by APCI, ESI or LSI mass spectrometry and the isotopic distribution of the $[M + 1]^+$ peaks is also in good agreement with the calculated spectra.

3.2. Electrochemical studies

The electrochemical properties of the complexes $[MO_2(L^n)]$ (M = Mo, W; n = 1–6, 9) were studied by cyclic voltammetry. Ferrocene was added as an internal reference in all measurements. The electrochemical data are summarized in Table 1. All these complexes exhibit an irreversible one-electron reduction process attributable to the conversion of M^{VI} to M^{V}. It is worth noting that the metal-based reduction potentials for the tungsten complexes are more negative by 0.29–0.50 V than those of the corresponding molybdenum counterparts. This is fully consistent with studies of other high-valent molybdenum and tungsten oxo-complexes [18a,41]. It can be seen that for the complexes $[MO_2(L^n)]$ (M = Mo, W; n = 1–3) the substituents on the phenolic ring of the ligands have marginal effects on the reduction potential

Table 1
Electrochemical data for $[MO_2(L^n)]$ (M = Mo, W; n = 1–6, 9)[a]

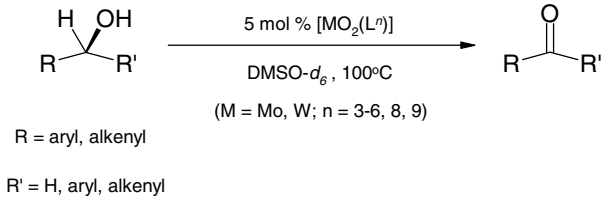
Compound	Reduction potential (V) vs. SCE	Process
$[MoO_2(L^1)]$	−1.41	Irreversible
$[MoO_2(L^2)]$	−1.42	Irreversible
$[MoO_2(L^3)]$	−1.44	Irreversible
$[MoO_2(L^4)]$	−1.45	Irreversible
$[MoO_2(L^5)]$	−1.65	Irreversible
$[MoO_2(L^6)]$	−1.31	Irreversible
$[MoO_2(L^9)]$	−1.02	Irreversible
$[WO_2(L^1)]$	−1.86	Irreversible
$[WO_2(L^2)]$	−1.89	Irreversible
$[WO_2(L^3)]$	−1.90	Irreversible
$[WO_2(L^4)]$	−1.92	Irreversible
$[WO_2(L^5)]$	−1.94	Irreversible
$[WO_2(L^6)]$	−1.81	Irreversible

[a] Recorded with $[Bu_4N][BF_4]$ as electrolyte in DMF (0.1 M) at ambient temperature. Scan rate 100 mV s^{-1}.

and are consistent with the electron donating character of the methyl and *tert*-butyl groups. They follow the order $[MoO_2(L^1)] > [MoO_2(L^2)] > [MoO_2(L^3)]$ as a result of the different electron donating abilities (^{t}Bu > Me > H). A similar trend can also be observed from the tungsten analogues.

It is interesting to note that incorporation of sulfur into the tetradentate ligand system as in L^6 lowers the reduction potential of the tungsten complex (−1.81 V versus SCE) relative to the analogous oxygen-containing ligands (−2.16 to −2.45 V versus SCE) [20a], although some caution is attached to discussion of irreversible processes such as those observed here. The reduction potential of $[WO_2(L^6)]$ having N_2S_2 coordination is lower than with N_2OS coordination by 0.05–0.13 V. However, $[WO_2(L^6)]$ is still more negative than those of the synthetic models for tungstoenzymes such as $[Et_4N]_2[WO_2(dtc)_2]$ (bdt = 1,2-benzenedithiolate) ($E_{pc} = -1.34$ V versus SCE) [18c] and $[Et_4N]_2[WO_2(mnt)_2]$ (mnt = 1,2-dicyanoethylenedithiolate) ($E_{pc} = -1.50$ V versus Ag/Ag^+ in MeCN) [18c].

The complex $[MoO_2(L^9)]$ exhibits an irreversible one-electron reduction process attributable to the Mo^{VI} to Mo^{V} process at $E_{pc} = -1.02$ V versus SCE in DMF. This data are fully consistent with that of $[MoO_2\{HN(CH_2CH_2S)_2\}]$ with $E_{pc} = -0.98$ V versus



Scheme 7.

Table 2
Percentage conversion of benzoin into benzil catalysed by $[MoO_2(L^n)]$[a]

Entry	Complex	Time (h)	Conversion (%)
1	$[MoO_2(L^3)]$	12	75
2	$[MoO_2(L^4)]$	12	81
3	$[MoO_2(L^5)]$	12	86
4	$[MoO_2(L^6)]$	6	98
5	$K[MoO_2(L^8)]$	12	79
6	$[MoO_2(L^9)]$	4	99
7	$[WO_2(L^3)]$	98	14
8	$[WO_2(L^4)]$	98	19
9	$[WO_2(L^5)]$	98	53
10	$[WO_2(L^6)]$	48	87
11	$K[WO_2(L^8)]$	98	44

[a] 5 mol% metal complex was treated with 0.2 mmol benzoin in deoxygenated DMSO-d_6 at 100 °C.

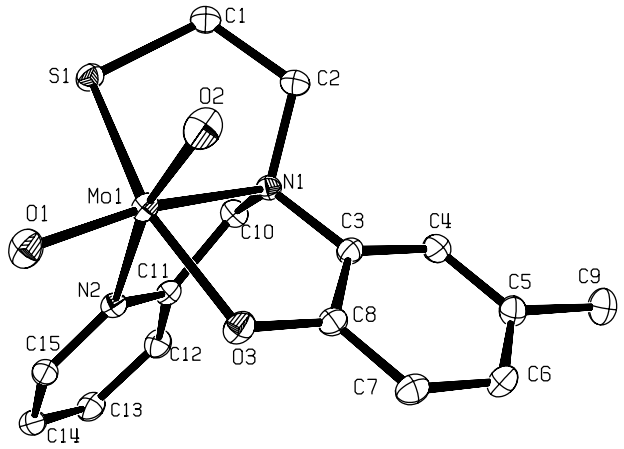


Fig. 1. Molecular structure and atom labeling scheme for $[MoO_2(L^2)]$. Hydrogen atoms are omitted for clarity.

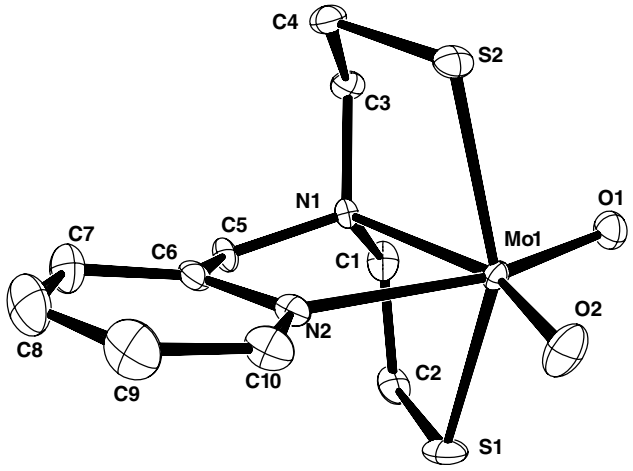


Fig. 2. Molecular structure and atom labeling scheme for $[MoO_2(L^6)]$. Hydrogen atoms are omitted for clarity.

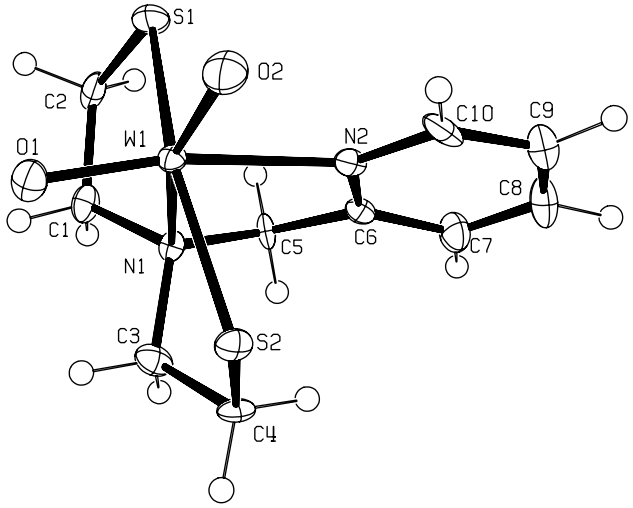


Fig. 3. Molecular structure and atom labeling scheme for $[WO_2(L^6)]$.

Table 3
Selected bond distances (Å) and angles (°) for complexes **[$MoO_2(L^2)$]**, **[$MoO_2(L^6)$]** and **[$WO_2(L^6)$]**

[$MoO_2(L^2)$]		**[$MoO_2(L^6)$]**		**[$WO_2(L^6)$]**	
Mo(1)–S(1)	2.3854(4)	Mo(1)–O(1)	1.7131(13)	W(1)–O(1)	1.732(4)
Mo(1)–O(1)	1.7069(12)	Mo(1)–O(2)	1.7065(14)	W(1)–O(2)	1.715(5)
Mo(1)–O(2)	1.7067(13)	Mo(1)–S(1)	2.4052(5)	W(1)–S(1)	2.4149(17)
Mo(1)–O(3)	2.0034(12)	Mo(1)–S(2)	2.4344(5)	W(1)–S(2)	2.4135(15)
Mo(1)–N(1)	2.3493(13)	Mo(1)–N(1)	2.3493(15)	W(1)–N(1)	2.328(5)
Mo(1)–N(2)	2.3606(14)	Mo(1)–N(2)	2.3797(15)	W(1)–N(2)	2.354(5)
S(1)–Mo(1)–O(1)	98.68(4)	S(1)–Mo(1)–S(2)	154.333(17)	S(1)–W(1)–S(2)	155.04(6)
S(1)–Mo(1)–O(2)	96.48(5)	S(1)–Mo(1)–O(1)	97.29(5)	S(1)–W(1)–O(1)	97.5(3)
O(1)–Mo(1)–O(2)	108.24(6)	S(2)–Mo(1)–O(1)	95.38(5)	S(2)–W(1)–O(1)	95.2(3)
S(1)–Mo(1)–O(3)	150.69(3)	S(1)–Mo(1)–O(2)	97.72(5)	S(1)–W(1)–O(2)	96.82(17)
O(1)–Mo(1)–O(3)	103.86(5)	S(2)–Mo(1)–O(2)	99.49(5)	S(2)–W(1)–O(2)	99.94(17)
O(2)–Mo(1)–O(3)	94.02(6)	O(1)–Mo(1)–O(2)	107.86(7)	O(1)–W(1)–O(2)	106.7(2)
S(1)–Mo(1)–N(1)	75.52(3)	S(1)–Mo(1)–N(1)	76.79(4)	S(1)–W(1)–N(1)	76.88(13)
O(1)–Mo(1)–N(1)	156.13(5)	S(2)–Mo(1)–N(1)	79.92(4)	S(2)–W(1)–N(1)	80.67(13)
O(2)–Mo(1)–N(1)	95.49(5)	O(1)–Mo(1)–N(1)	95.16(5)	O(1)–W(1)–N(1)	95.24(18)
O(3)–Mo(1)–N(1)	76.29(5)	O(2)–Mo(1)–N(1)	156.89(6)	O(2)–W(1)–N(1)	80.67(13)
S(1)–Mo(1)–N(2)	84.89(3)	S(1)–Mo(1)–N(2)	83.96(4)	S(1)–W(1)–N(2)	83.81(12)
O(1)–Mo(1)–N(2)	85.89(5)	S(2)–Mo(1)–N(2)	78.57(4)	S(2)–W(1)–N(2)	79.04(12)
O(2)–Mo(1)–N(2)	165.34(5)	O(1)–Mo(1)–N(2)	166.14(6)	O(1)–W(1)–N(2)	166.8(2)
O(3)–Mo(1)–N(2)	78.37(5)	O(2)–Mo(1)–N(2)	85.56(6)	O(2)–W(1)–N(2)	86.1(2)
N(1)–Mo(1)–N(2)	70.65(5)	N(1)–Mo(1)–N(2)	71.62(5)	N(1)–W(1)–N(2)	72.21(16)

Table 4
Crystallographic data for **[$MoO_2(L^2)$]**, **[$MoO_2(L^6)$]** and **[$WO_2(L^6)$]**

	[$MoO_2(L^2)$]	**[$MoO_2(L^6)$]**	**[$WO_2(L^6)$]**
Empirical formula	$C_{15}H_{16}MoN_2O_3S$	$C_{10}H_{14}MoN_2O_2S_2$	$C_{10}H_{14}N_2O_2S_2W$
Formula weight	400.30	354.29	442.20
Diffractometer	Enraf-Nonius KappaCCD	Enraf-Nonius DIP2000	Enraf-Nonius KappaCCD
Temperature (K)	150	150	150
Colour	yellow plate	orange block	yellow block
Crystal size (mm^3)	0.1×0.3×0.3	0.3×0.3×0.4	0.06×0.14×0.20
Crystal system	triclinic	orthorhombic	orthorhombic
Space group	$P\bar{1}$ (No. 2)	$Pna2_1$ (No. 33)	$Pna2_1$ (No. 33)
a (Å)	6.6900(1)	12.963(1)	8.6513(3)
b (Å)	7.3783(2)	11.416(1)	11.4311(3)
c (Å)	16.7711(5)	8.667(1)	12.9956(5)
α (°)	78.347(1)	90	90
β (°)	78.495(1)	90	90
γ (°)	71.845(1)	90	90
V ($Å^3$)	762.1	1282.6	1285.2
Z	2	4	4
D_{calc} (Mg/m^3)	1.74	1.83	2.29
μ (mm^{-1})	1.01	1.34	9.30
$F(000)$	400.56	705.51	835.59
λ (Mo Kα) (Å)	0.71073	0.71069	0.71073
Transmission coefficients (min, max)	0.74, 0.90	0.56, 0.67	0.27, 0.57
θ Range for data collection (°)	$0 \leqslant \theta \leqslant 27.5$	$0 \leqslant \theta \leqslant 26.37$	$0 \leqslant \theta \leqslant 27.5$
Number of data measured	10645	8227	8378
Number of unique data (R_{int})	3248 (0.017)	2491 (0.021)	2904 (0.042)
Number of observed data ($I > 3\sigma(I)$)	3139	2485	2399
Number of parameters, p	199	155	155
R	0.0247	0.0186	0.0239
R_w	0.0254	0.0184	0.0244
S(GOF)	1.0502	0.9952	1.0430
Largest difference peak and hole (e $Å^{-3}$)	+0.45 and −0.61	+0.51 and −1.16	+1.50 and −1.63

SCE in DMSO [42]. It is worth noting that this five-coordinate dioxomolybdenum complex has remarkably lower reduction potential by ca 0.3 V compared to that of $[MoO_2(L^6)]$ ($E_{pc} = -1.31$ V versus SCE in DMF) which adopts a six-coordinate geometry, and is significantly lower than those dioxomolybdenum(VI) complexes containing N_2OS tetradentate ligands ($E_{pc} = -1.41$ to -1.65 V versus SCE).

3.3. Oxidation catalysis studies

As indicated above, the vast majority of the homogeneous metal-based alcohol oxidation systems studied to date have involved the use of peroxide or hydroperoxides as oxidants. There have also been a number of studies where coupled systems involving electron transfer agents in tandem with a metal complex for oxidation of alcohols using oxygen as the oxidant [43]. The use of $[RuO_4]^-$ in the presence of copper salts [44] and OsO_4 with dimethylsulfoxide (DMSO) as co-oxidant [45] as homogeneous oxidants for alcohols have also been reported. There is also one example of the use of $[MoO_2(acac)_2]$ in the presence of DMSO, but ligand effects were not studied nor was the activity of comparable tungsten complexes [46]. We here report briefly the activity of the dioxo complexes $[MO_2(L^n)]$ (M = Mo, W; n = 3–6, 8, 9) for the catalytic oxidation of primary or secondary allylic and benzylic alcohols with DMSO as the oxo-donor (see Scheme 7).

In a typical experiment, 5 mol% of the complex and 0.2 mmol of benzoin were dissolved in deoxygenated DMSO-d_6 (0.5 ml). The mixture was sealed in a NMR tube and heated at 100 °C. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. All of the complexes were initially screened for their ability to oxidise benzoin and the complex $[MoO_2(L^9)]$ was found to be the most active. The results were summarized in Table 2. The molybdenum analogues gave much higher conversions in shorter reaction times than tungsten, consistent with the lower metal-based reduction potentials of the molybdenum complexes relative to those of tungsten. The donor groups were one of the major factors that affected the performance of the catalyst and complexes having ligands with more than one sulfur donor showed significantly better performance. There were also minor effects due to variations of substituents on the ligand aryl groups.

We then investigated the activity of the complex $[MoO_2(L^9)]$ in DMSO for the oxidation of a range of primary and secondary allylic and benzylic alcohols. [1] Yields in the range 68–99% were obtained. Substrates containing phenolic OH or aromatic NO_2 substituents could also be oxidised in good yields.

Apart from the small scale reactions (0.2 mmol), this catalytic oxidation system has been proved to be successful on a larger scale. A 10 mmol reaction of benzoin, 2-hydroxybenzyl alcohol and *trans*-cinnamyl alcohol provided benzil, salicylaldehyde and *trans*-cinnamaldehyde in 95%, 83%, 94% isolated yields, respectively.

[1] Substrates used in the catalytic activity studies of $[MoO_2(L^9)]$ (product, % yield, reaction time): benzoin (benzil, 99%, 3 h), benzhydrol (benzophenone, 80%, 18 h), *trans*-cinnamyl alcohol (*trans*-cinnamaldehyde, 99%, 18 h), 2-hydroxybenzyl alcohol (salicylaldehyde, 89%, 24 h), 4-hydroxybenzyl alcohol (4-hydroxybenzaldehyde, 94%, 24 h), 4-methylbenzyl alcohol (*p*-tolualdehyde, 98%, 24 h), 4-*tert*-butylbenzyl alcohol (4-*tert*-butylbenzaldehyde, 78%, 24 h), 4-methoxybenzyl alcohol (4-methoxybenzaldehyde, 68%, 24 h), 4-chlorobenzyl alcohol (4-chlorobenzaldehyde, 95%, 24 h) and 4-nitrobenzyl alcohol (4-nitrobenzaldehyde, 99%, 20 h).

3.4. X-ray structural studies

The molecular structures of $[MoO_2(L^2)]$, $[MoO_2(L^6)]$ and $[WO_2(L^6)]$ were established by single-crystal X-ray diffraction analysis and the perspective views of these structures are shown in Figs. 1–3, respectively. Selected bond distances and angles for these complexes are summarized in Table 3 and crystallographic data in Table 4. $[MoO_2(L^2)]$ crystallizes in the triclinic space group $P\bar{1}$. Since ligand L^2 possesses three different pendant arms, the complex $[MoO_2(L^2)]$ is prochiral. One of the two enantiomeric isomers in the unit cell is depicted in Fig. 1. $[MoO_2(L^6)]$ and $[WO_2(L^6)]$ are isomorphous and crystallize in the orthorhombic space group $Pna2_1$. The overall geometry of these three compounds about the metal centre is pseudo-octahedral with the two oxo-groups in the usual *cis* configuration and *trans* to the two nitrogen donor atoms of the ligand. The five member chelate ring systems of these three complexes cause a bending of the NOS/NSS donor set away from the oxo-groups which have an O–Mo–O angle of 107.9–108.2° and O–W–O angle of 106.7°. The Mo═O bond distances (1.694–1.713 Å) and W═O bond distances (1.715–1.732 Å) are within the range typical for oxo-molybdenum [20a,38] and oxo-tungsten species [47,48]. The Mo–S single bond distances (2.347–2.434 Å) and W–S single bond distances (2.414–2.415 Å) are comparable to those in other Mo(VI) and W(VI) thiolates [38].

4. Conclusions

A series of new asymmetric potentially dianionic or trianionic tetradentate proligands have been synthesised using both modification of known methods or new synthetic routes. Their coordination chemistry has been initially explored by reaction with $[MoO_2(acac)_2]$ or $[WO_2Cl_2(dme)]$ to give a series of dioxo-complexes of the type $[MO_2(L)]^{n-}$ (n = 0, 1). Variation of chelate ring size and donor atom was shown to have relatively little impact on the standard bond distances and bond angles for the dioxo-complexes. The complexes have been shown to be efficient catalysts for the oxidation of primary and secondary allylic and benzylic alcohols in good but unexceptional yields.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.ica.2004.07.008.

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