

# *cis*-Dioxo-tungsten(VI) and -molybdenum(VI) complexes with $N_2O_2$ tetradentate ligands: synthesis, structure, electrochemistry and oxo-transfer properties

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Treatment of  $[WO_2Cl_2(dme)]$  with  $N_2O_2$  tetradentate ligands  $[H_2L^n (n = 1-7)]$  in the presence of 2 equivalents of triethylamine gave the corresponding dioxotungsten(VI) complexes  $[WO_2L^n] (n = 1-7)$ . The molybdenum counterparts  $[MoO_2L^n] (n = 1-4)$  were prepared in good yield by treating ammonium molybdate tetrahydrate with the respective ligands and dilute hydrochloric acid. The molecular structures of four of these complexes, namely  $[WO_2L^n] (n = 1, 5 \text{ or } 6)$  and  $[MoO_2L^2]$ , as determined by single crystal X-ray analysis, revealed that the metal centre exhibits distorted octahedral co-ordination with *cis*-dioxo ligands. These high-valent oxo complexes are active toward oxygen atom transfer reactions and can catalyse the oxidation of benzoin with dmsO. Their reactivity and electrochemical properties are discussed and compared.

High-valent molybdenum and tungsten complexes with oxo ligation have attracted considerable attention in the recent literature.<sup>1</sup> Apart from their intrinsic interest, the chemistry of these complexes has been developed with a view to gaining a better understanding concerning their role in various industrial and biological processes. It is well documented that high-valent molybdenum and tungsten compounds can act as catalysts for olefin metathesis reactions<sup>2</sup> and are also involved in various oxidation processes.<sup>3</sup> Such compounds with dithiolene-type ligands are also related to a class of enzymes known as oxotransferases, which catalyse oxygen atom transfer to and from a substrate.<sup>4,5</sup> While the relevant molybdenum chemistry is well developed and numerous oxomolybdenum complexes with a range of supporting ligands have been studied extensively,<sup>6</sup> the chemistry of analogous tungsten complexes remains relatively little studied although substantial recent progress has been stimulated by the unique nature and properties of tungsten-containing enzymes.<sup>7-14</sup> In this paper we describe the preparation and characterization of a series of *cis*-dioxo-tungsten(VI) compounds containing  $N_2O_2$  tetradentate ligands with different co-ordination modes, together with their electrochemistry and reactivity toward oxo-transfer reactions. The analogous molybdenum complexes have also been studied and a comparison made between these two series of compounds including their structures and properties.

## Experimental

### General procedures

All reactions were carried out using standard Schlenk-line techniques under an atmosphere of nitrogen; work-ups were performed in air. Dichloromethane was dried over 4 Å molecular sieves and distilled from calcium hydride. Tetrahydrofuran (thf) was distilled from sodium-benzophenone. Dimethylformamide (dmf) for voltammetric studies was dried over barium oxide and distilled under reduced pressure. The electrolyte  $[NBu_4][ClO_4]$  was recrystallized from dry acetone three times prior to use. All other reagents and solvents were of reagent grade and used as received. The ligands  $H_2L^n (n = 1, 2, 5 \text{ or } 6)$ <sup>15,16</sup> and the tungsten complex  $[WO_2Cl_2(dme)]$ <sup>17</sup> were prepared according to literature procedures.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker DPX 300 spectrometer (<sup>1</sup>H, 300; <sup>13</sup>C, 75.4 MHz) in CD<sub>3</sub>SOCD<sub>3</sub> solutions unless otherwise stated. Chemical shifts were relative to internal SiMe<sub>4</sub> (δ 0). The IR spectra were taken on a Nicolet Magna 550 FT-IR spectrometer as KBr pellets. Liquid secondary-ion (LSI) and FAB mass spectra were measured on a Bruker APEX 47e Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer or a Hewlett-Packard 5989B mass spectrometer, respectively, with 3-nitrobenzyl alcohol as matrix. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

Electrochemical measurements were carried out on a BAS CV-50W voltammetric analyser. The cell comprised inlets for a platinum-sphere working electrode, a silver-wire counter electrode and a Ag-AgNO<sub>3</sub> (0.1 mol dm<sup>-3</sup> in MeCN) reference electrode which was connected to the solution by a Luggin capillary whose tip was placed close to the working electrode.<sup>18</sup> Typically, a 0.1 mol dm<sup>-3</sup> solution of  $[NBu_4][ClO_4]$  in dmf containing 1.0 mmol dm<sup>-3</sup> of sample was purged with nitrogen for 20 min, then the voltammograms were recorded at scan rates ranging from 20 to 3000 mV s<sup>-1</sup> at ambient temperature. Ferrocene was also added as an internal reference and all potentials are reported with respect to the Ag-Ag<sup>+</sup> couple in MeCN.

### Preparations

**2-[Bis(2-hydroxybenzyl)aminomethyl]pyridine ( $H_2L^1$ ).**<sup>15</sup> To a solution of 2-(aminomethyl)pyridine (2.16 g, 20 mmol) in MeOH (50 cm<sup>3</sup>) was added salicylaldehyde (2.44 g, 20 mmol). The yellow Schiff base product appeared immediately and the mixture was kept stirring for 2 h at room temperature (r.t.). Sodium tetrahydroborate (0.76 g, 20 mmol) was then added slowly and stirring was continued for 1 h. The volatiles of the mixture were removed under reduced pressure and the residue was mixed with water (50 cm<sup>3</sup>). The mixture was then neutralized with acetic acid before being extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 cm<sup>3</sup>). The combined extracts was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to give the monocondensed product 2-(2-hydroxybenzylaminomethyl)pyridine ( $H_2L^8$ ), which could be purified by column chromatography with ethyl acetate as eluent (3.85 g, 90% yield). The crude product was dissolved again in MeOH (50 cm<sup>3</sup>) and salicylaldehyde (2.44 g, 20 mmol) added.

The mixture was stirred at r.t. for 2 h, then NaBH<sub>4</sub> (0.76 g, 20 mmol) added. The mixture was kept stirring for 1 h and the volatiles were removed *in vacuo*. The residue was dissolved in water (50 cm<sup>3</sup>) and then neutralized with acetic acid. The resulting mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 cm<sup>3</sup>) and the combined extracts dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated, then loaded onto a silica gel column which was eluted with CH<sub>2</sub>Cl<sub>2</sub> followed by ethyl acetate. The second band was collected and evaporated to give a white solid which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>. Yield: 2.88 g (45%), mp 168–169 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.66 (d, *J* = 4.5, 1 H, py), 7.71 (dt, *J* = 1.7, 7.7, 1 H, py), 7.31–7.26 (m, 1 H, py), 7.21–7.13 (m, 3 H, aryl and py), 7.07 (dd, *J* = 1.4, 7.4, 2 H, aryl), 6.90 (dd, *J* = 0.8, 8.1, 2 H, aryl), 6.79 (dt, *J* = 1.0, 7.4 Hz, 2 H, aryl), 3.91 (s, 2 H, C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>) and 3.84 (s, 4 H, C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>).

**2-[(2-Hydroxybenzyl)(2-hydroxy-5-nitrobenzyl)aminomethyl]pyridine (H<sub>2</sub>L<sup>3</sup>).** To a solution of 2-hydroxy-5-nitrobenzyl chloride (0.56 g, 3 mmol) in thf (30 cm<sup>3</sup>) were added H<sub>2</sub>L<sup>8</sup> (0.64 g, 3 mmol) and triethylamine (0.4 cm<sup>3</sup>, 3 mmol). The mixture was refluxed overnight to give a yellow suspension which was cooled and filtered. The filtrate was concentrated and chromatographed using CHCl<sub>3</sub> as eluent. The first band was collected and evaporated to give the product as a yellow solid. Yield: 0.84 g (77%), mp 141–142 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.67 (dd, *J* = 0.6, 5.1, 1 H, py), 8.10 (dd, *J* = 3.0, 9.0, 1 H, aryl), 8.05 (d, *J* = 3.0, 1 H, aryl), 7.77 (dt, *J* = 1.7, 7.7, 1 H, py), 7.36–7.32 (m, 1 H, py), 7.22–7.16 (m, 2 H, aryl and py), 7.08 (dd, *J* = 1.5, 7.5, 1 H, aryl), 6.96 (d, *J* = 9.0, 1 H, aryl), 6.87 (dd, *J* = 1.0, 8.1, 1 H, aryl), 6.81 (dt, *J* = 1.0, 7.5, 1 H, aryl), 3.98 (s, 2 H, CH<sub>2</sub>), 3.91 (s, 2 H, CH<sub>2</sub>) and 3.89 (s, 2 H, CH<sub>2</sub>). <sup>13</sup>C-<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 163.9, 157.0, 155.5, 148.0, 140.0, 138.1, 130.3, 129.7, 126.5, 125.9, 123.4, 123.0, 122.0, 120.8, 119.5, 117.6, 117.0, 56.8, 56.3 and 56.0 (Found: C, 65.65; H, 5.29; N, 11.48. Calc. for C<sub>20</sub>H<sub>19</sub>N<sub>3</sub>O<sub>4</sub>: C, 65.74; H, 5.24; N, 11.50%).

**2-(3,5-Di-*tert*-butyl-2-hydroxybenzylaminomethyl)pyridine (H<sub>2</sub>L<sup>9</sup>).** 3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (1.17 g, 5 mmol) was added to a stirred solution of 2-(aminomethyl)pyridine (0.54 g, 5 mmol) in MeOH (30 cm<sup>3</sup>). The yellow Schiff base product appeared immediately and stirring was continued for 1 h at r.t. Sodium tetrahydroborate (0.19 g, 5 mmol) was then added slowly and the mixture stirred for 4 h. The volatiles were removed *in vacuo* and the residue was dissolved in water (30 cm<sup>3</sup>). The mixture was then neutralized with acetic acid and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 cm<sup>3</sup>). The combined extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated and chromatographed using ethyl acetate as eluent. The first band was collected and evaporated to give a pale yellow solid. Yield: 1.62 g (99%), mp 71–74 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.56 (d, *J* = 4.5, 1 H, py), 7.64 (dt, *J* = 1.7, 7.7, 1 H, py), 7.24–7.17 (m, 3 H, aryl and py), 6.84 (d, *J* = 2.4 Hz, 1 H, aryl), 3.98 (s, 2 H, CH<sub>2</sub>), 3.93 (s, 2 H, CH<sub>2</sub>), 1.44 (s, 9 H, Bu<sup>t</sup>) and 1.28 (s, 9 H, Bu<sup>t</sup>). <sup>13</sup>C-<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 157.9, 154.6, 149.4, 140.4, 136.6, 135.8, 123.4, 123.0, 122.6, 122.3, 121.7, 53.3, 52.7, 34.9, 34.1, 31.6 and 29.6.

**2-[(3,5-Di-*tert*-butyl-2-hydroxybenzyl)(2-hydroxy-5-nitrobenzyl)aminomethyl]pyridine (H<sub>2</sub>L<sup>4</sup>).** According to the procedure described for H<sub>2</sub>L<sup>3</sup>, this ligand was prepared from 2-hydroxy-5-nitrobenzyl chloride (0.75 g, 4 mmol) and H<sub>2</sub>L<sup>9</sup> (1.30 g, 4 mmol) as a yellow solid. Yield: 1.57 g (82%), mp 87–90 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.67 (dd, *J* = 0.6, 5.1, 1 H, py), 8.12–8.07 (m, 2 H, aryl), 7.77 (t, *J* = 7.8, 1 H, py), 7.37–7.35 (m, 1 H, py), 7.24–7.20 (m, 2 H, aryl and py), 6.95 (d, *J* = 8.7, 1 H, aryl), 6.89 (d, *J* = 2.4 Hz, 1 H, aryl), 3.94 (s, 2 H, CH<sub>2</sub>), 3.90 (s, 2 H, CH<sub>2</sub>), 3.86 (s, 2 H, CH<sub>2</sub>), 1.38 (s, 9 H, Bu<sup>t</sup>) and 1.27 (s, 9 H, Bu<sup>t</sup>). <sup>13</sup>C-<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 163.9, 155.5, 153.5, 147.8, 140.9, 140.0, 138.1, 136.3, 127.2, 125.8, 124.6, 123.8, 123.7, 123.0, 122.2, 120.3, 117.8, 58.1, 55.7, 55.3, 35.0, 34.1, 31.6

and 29.6. HRMS (LSI): *m/z* calc. for C<sub>28</sub>H<sub>36</sub>N<sub>3</sub>O<sub>4</sub> [M + H]<sup>+</sup>, 478.2706, found 478.2683.

***N,N'*-Bis(2-hydroxy-5-nitrobenzyl)-*N,N'*-dimethylethane-1,2-diamine (H<sub>2</sub>L<sup>7</sup>).** To a solution of 2-hydroxy-5-nitrobenzyl chloride (1.12 g, 6 mmol) in thf (50 cm<sup>3</sup>) were added *N,N'*-dimethylethane-1,2-diamine (0.26 g, 3 mmol) and triethylamine (0.83 cm<sup>3</sup>, 6 mmol). The mixture was refluxed overnight to give a yellow suspension which was cooled and filtered. The filtrate was rotary evaporated to give a yellow solid which was washed thoroughly with diethyl ether then recrystallized from CH<sub>2</sub>Cl<sub>2</sub>–hexane. Yield: 1.03 g (88%), mp 192–196 °C. <sup>1</sup>H NMR: δ 8.11 (d, *J* = 3.0, 2 H, aryl), 8.00 (dd, *J* = 3.0, 9.0, 2 H, aryl), 6.78 (d, *J* = 9.0 Hz, 2 H, aryl), 4.08 (br s, 2 H, OH), 3.75 (s, 4 H, C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>), 2.78 (s, 4 H, CH<sub>2</sub>CH<sub>2</sub>) and 2.26 (s, 6 H, CH<sub>3</sub>). <sup>13</sup>C-<sup>1</sup>H} NMR: δ 166.2, 137.9, 126.5, 125.5, 123.6, 116.5, 56.2, 52.8 and 40.9. HRMS (LSI): *m/z* calc. for C<sub>18</sub>H<sub>23</sub>N<sub>4</sub>O<sub>6</sub> [M + H]<sup>+</sup>, 391.1617, found 391.1546.

**General procedure for the preparation of [WO<sub>2</sub>L<sup>*n*</sup>] (*n* = 1–7).** To a mixture of [WO<sub>2</sub>Cl<sub>2</sub>(dme)] (0.38 g, 1.0 mmol) and H<sub>2</sub>L<sup>*n*</sup> (*n* = 1–7) (1.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (*ca.* 30 cm<sup>3</sup>) was added triethylamine (0.28 cm<sup>3</sup>, 2.0 mmol). The mixture was refluxed overnight, then concentrated and chromatographed using CH<sub>2</sub>Cl<sub>2</sub> (for *n* = 1 or 4), CHCl<sub>3</sub> (for *n* = 3) or ethyl acetate (for *n* = 5 or 6) as eluent. The complexes [WO<sub>2</sub>L<sup>*n*</sup>] (*n* = 2 or 7) were only sparingly soluble in CH<sub>2</sub>Cl<sub>2</sub> and were purified by filtration followed by washing with CH<sub>2</sub>Cl<sub>2</sub>, diethyl ether and hexane. The other tungsten complexes were further purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>–hexane.

**General procedure for the preparation of [MoO<sub>2</sub>L<sup>*n*</sup>] (*n* = 1–4).** A mixture of ammonium molybdate tetrahydrate [NH<sub>4</sub>]<sub>6</sub>[Mo<sub>7</sub>O<sub>24</sub>]·4H<sub>2</sub>O (0.18 g, 0.14 mmol), H<sub>2</sub>L<sup>*n*</sup> (*n* = 1–4) (1.0 mmol) and dilute hydrochloric acid (0.1 M, 5 cm<sup>3</sup>, 0.5 mmol) in EtOH (40 cm<sup>3</sup>) was stirred at r.t. overnight. For [MoO<sub>2</sub>L<sup>*n*</sup>] (*n* = 1–3) a yellow solid was collected after filtration which was washed with EtOH, diethyl ether and hexane, then dried *in vacuo*. The orange *tert*-butyl analogue [MoO<sub>2</sub>L<sup>4</sup>] was obtained by chromatography with CHCl<sub>3</sub> as eluent.

#### X-Ray crystallographic analysis of [WO<sub>2</sub>L<sup>*n*</sup>] (*n* = 1, 5 or 6) and [MoO<sub>2</sub>L<sup>2</sup>]

Crystal data and data processing parameters are given in Table 2. Data collection was performed at 293 K on a MSC/Rigaku RAXIS IIc imaging-plate system using Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) from a Rigaku RU-200 rotating-anode generator operating at 50 kV and 90 mA {for [WO<sub>2</sub>L<sup>1</sup>], 3° oscillation frames in the range of 0–159°, exposure 8 min per frame; for [WO<sub>2</sub>L<sup>5</sup>], 5° oscillation frames in the range of 0–150°, exposure 5 min per frame; for [WO<sub>2</sub>L<sup>6</sup>] and [MoO<sub>2</sub>L<sup>2</sup>], 3° oscillation frames in the range of 0–150°, exposure 8 min per frame}.<sup>19</sup> A self-consistent semiempirical absorption correction based on Fourier coefficient fitting of symmetry-equivalent reflections was applied by using the ABSCOR program.<sup>20</sup>

The structures were solved by direct methods, which yielded the positions of all non-hydrogen atoms, which were refined anisotropically. Hydrogen atoms in [WO<sub>2</sub>L<sup>1</sup>] were also located by subsequent Fourier difference syntheses, while those in the remaining three structures were placed in their idealized positions (C–H 0.96 Å) with fixed isotropic thermal parameters and allowed to ride on their parent carbon atoms. All the H atoms were held stationary and included in structure factor calculations in the final stage of full-matrix least squares refinement.

All computations were performed on an IBM-compatible personal computer with SHELXTL PC<sup>21</sup> (for structure solution) and SHELXL 93<sup>22</sup> (for refinement) program packages.

CCDC reference number 186/1095.

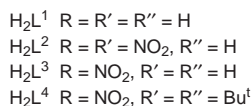
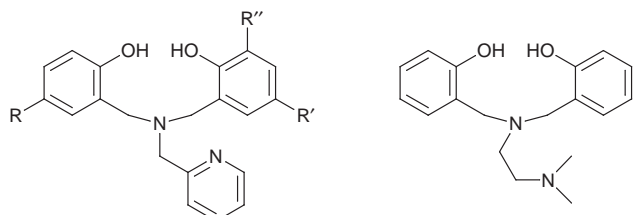
See <http://www.rsc.org/suppdata/dt/1998/3057/> for crystallographic files in .cif format.

## Results and discussion

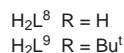
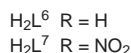
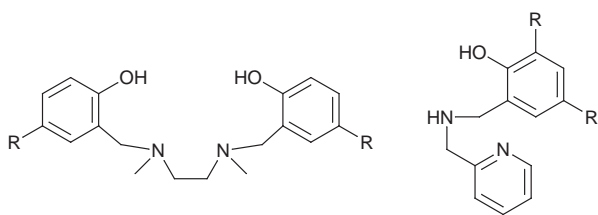
### Synthesis and spectroscopic characterization

The ligands  $H_2L^n$  ( $n = 1, 5$  or  $6$ ) were prepared previously by reductive amination starting from salicylaldehyde and the corresponding amines.<sup>15</sup> By using the stronger reducing agent  $NaBH_4$  under neutral conditions instead of  $NaBH_3(CN)$  at pH 5, we found that the reaction time could be significantly shortened and the yield of ligand  $H_2L^1$  was greatly increased from 3.8 to 45%. This simplified procedure is described in detail in the Experimental section. The ligand  $H_2L^2$  was synthesized by treating 2-(aminomethyl)pyridine with 2-hydroxy-5-nitrobenzyl chloride in the presence of triethylamine.<sup>16</sup> These two methodologies can be integrated to prepare unsymmetrical ligands such as  $H_2L^n$  ( $n = 3$  or  $4$ ). Thus reductive amination using 2-(aminomethyl)pyridine and 1 equivalent of salicylaldehyde or 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde gave the respective secondary amines  $H_2L^n$  ( $n = 8$  or  $9$ ), which underwent nucleophilic substitution with 2-hydroxy-5-nitrobenzyl chloride to give  $H_2L^n$  ( $n = 3$  or  $4$ ) in good yield. The ligand  $H_2L^7$  was prepared similarly from *N,N'*-dimethylethane-1,2-diamine and 2 equivalents of 2-hydroxy-5-nitrobenzyl chloride.

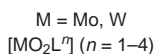
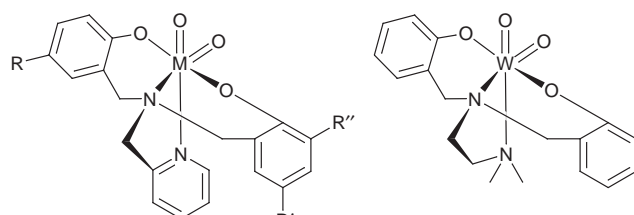
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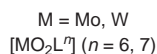
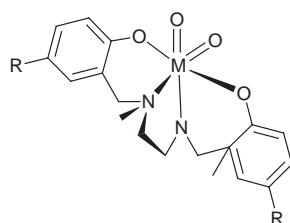
$H_2L^5$



Complexes:



$[WO_2L^5]$



The tungsten(vi) compounds  $Na_2WO_4 \cdot 2H_2O$ ,<sup>11,14</sup>  $WO_2Cl_2$ ,<sup>12,23</sup> and  $[WO_2(acac)_2]$ <sup>7a,23b,24</sup> are commonly used to prepare other dioxotungsten(vi) complexes. These starting materials, however, have some limitations. The first reagent can only be used in an acidic medium in which the species  $[WO_2]^{2+}$  is generated. Reactions employing this reagent appear to be susceptible to the pH of the reaction mixtures.<sup>25</sup> The complex  $WO_2Cl_2$  possesses a polymeric structure which renders it insoluble in most organic solvents.<sup>16</sup> Although its derivative  $[WO_2(acac)_2]$  has better solubility, its preparation is not always reproducible.<sup>7a</sup> The dme adduct  $[WO_2Cl_2(dme)]$  was first reported by Andersson and co-workers in 1991.<sup>17</sup> In contrast to  $WO_2Cl_2$  and its derivatives  $[WO_2Cl_2L_2]$  [ $L = dmf, dmsO, MeCN, Ph_3PO, etc.$ ],<sup>26</sup> this compound is highly soluble in organic solvents such as  $CH_2Cl_2$ ,  $MeCN$  and  $dmf$ . The dme and Cl ligands are also labile and can be displaced readily.<sup>27</sup> It thus serves as a good alternative as the starting material for other tungsten(vi) compounds. We employed this reagent to complex with the tetradentate ligands  $H_2L^n$  ( $n = 1-7$ ). Treatment of  $[WO_2Cl_2(dme)]$  with 1 equivalent of the ligand and 2 of triethylamine in  $CH_2Cl_2$  produced the corresponding  $[WO_2L^n]$  in moderate to good yields (Table 1). All of these tungsten(vi) complexes are air-stable and white except for  $[WO_2L^4]$  which is pale yellow.

The molybdenum counterparts  $[MoO_2L^n]$  ( $n = 1-4$ ) were also prepared for comparison. The synthesis involved the treatment of ammonium molybdate tetrahydrate with the ligands  $H_2L^n$  ( $n = 1-4$ ) in the presence of  $HCl$  in  $EtOH$ .<sup>28</sup> Filtration followed by washing with organic solvents led to the isolation of pure  $[MoO_2L^n]$  ( $n = 1-3$ ). The unsubstituted  $[MoO_2L^1]$  was prepared previously by using  $[MoO_2(acac)_2]$  as the starting material.<sup>15</sup> The *tert*-butyl analogue  $[MoO_2L^4]$  was purified readily by chromatography. All these molybdenum complexes are also stable to air.

Purification of the dinitro complexes  $[WO_2L^n]$  ( $n = 2$  or  $7$ ) was found to be rather difficult because of the poor solubility in organic solvents. In contrast, the ligand  $H_2L^4$  and its molybdenum and tungsten complexes  $[MO_2L^4]$  ( $M = Mo$  or  $W$ ) were highly soluble and could be purified by chromatography. Although the  $^1H$  NMR spectra of all these compounds suggested that the samples were essentially pure, the analytical data were still not entirely satisfactory even after repeating the chromatographic procedure and recrystallization. These compounds, however, were unambiguously characterized with accurate mass measurements together with other spectroscopic techniques. Table 1 summarizes the analytical and spectroscopic data for the dioxo complexes  $[WO_2L^n]$  ( $n = 1-7$ ) and  $[MoO_2L^n]$  ( $n = 2-4$ ).

The IR spectra of all these dioxo compounds showed two strong bands within 907–914 and 934–949  $cm^{-1}$  attributable to the asymmetric and symmetric  $M=O$  stretches, respectively in a *cis*-dioxo moiety.<sup>9b,10d</sup> The only exceptions were those for  $[MoO_2L^2]$  and  $[MoO_2L^4]$ , which exhibited only one strong and broad band at 918 or 910  $cm^{-1}$ , respectively. There was no difference in these stretching frequencies between the molybdenum and tungsten complexes of  $H_2L^3$ . The spectra of compounds containing nitro group(s) also displayed strong bands at 1333–1343 and 1510–1518  $cm^{-1}$  which arise from the  $C-NO_2$  stretching vibrations.<sup>29</sup> The  $^1H$  and  $^{13}C$  NMR data for these complexes were in accord with the proposed octahedral structure shown. For complexes with a symmetrical ligand, they possess either an internal mirror plane,  $[WO_2L^n]$  ( $n = 1, 2$  or  $5$ ) and  $[MoO_2L^2]$ , or a  $C_2$  rotation axis,  $[WO_2L^n]$  ( $n = 6$  or  $7$ ). Upon complexation the two methylene protons next to the benzene ring are no longer equivalent as expected. For example, two doublets at  $\delta$  4.83 and 4.33, both with a geminal coupling constant of 14.4 Hz, appeared in the  $^1H$  NMR spectrum of  $[WO_2L^2]$  recorded in  $CD_3SOCD_3$ . For complexes with an unsymmetrical ligand such as  $[MO_2L^n]$  ( $M = Mo$  or  $W$ ,  $n = 3$  or  $4$ ), up to four doublets could be resolved for these  $CH_2$  protons. All these complexes were also characterized with mass spec-

**Table 1** Analytical and spectroscopic data for [WO<sub>2</sub>L<sup>n</sup>] (*n* = 1–7) and [MoO<sub>2</sub>L<sup>n</sup>] (*n* = 2–4)

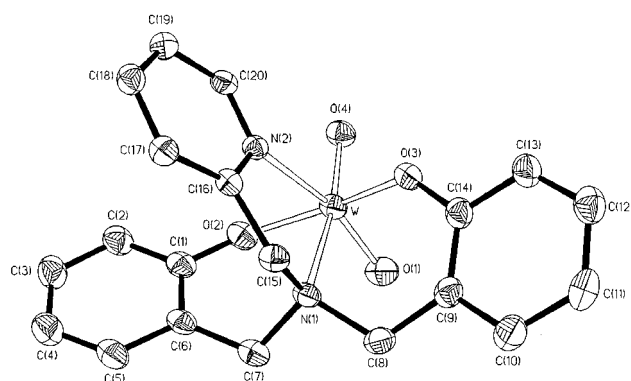
Compound	Yield (%)	Analysis <sup>a</sup> (%)			Spectroscopic data <sup>b</sup>
		C	H	N	
[WO <sub>2</sub> L <sup>1</sup> ]	48	44.29 (44.97)	3.21 (3.40)	5.07 (5.24)	<sup>1</sup> H NMR: δ 8.95 (d, <i>J</i> = 5.4, 1 H, py), 7.79 (dt, <i>J</i> = 1.3, 7.7, 1 H, py), 7.40 (t, <i>J</i> = 6.5, 1 H, py), 7.19 (d, <i>J</i> = 7.5, 2 H, aryl), 7.09–7.04 (m, 3 H, aryl and py), 6.77 (t, <i>J</i> = 7.5, 2 H, aryl), 6.52 (d, <i>J</i> = 8.1, 2 H, aryl), 4.75 (d, <i>J</i> = 13.5, 2 H, C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> ), 4.09–4.05 (m, 4 H, C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> and C <sub>5</sub> H <sub>4</sub> CH <sub>2</sub> ) <sup>13</sup> C- <sup>1</sup> H NMR: δ 160.7, 156.2, 150.4, 140.9, 129.7, 129.4, 124.3, 123.2, 123.1, 120.8, 118.3, 61.6, 58.6 IR: ν(WO <sub>2</sub> ) 937s, 907s MS (FAB): a cluster peaking at <i>m/z</i> 535 (100%), [M + H] <sup>+</sup>
[WO <sub>2</sub> L <sup>2</sup> ]	83				<sup>1</sup> H NMR: δ 9.00 (d, <i>J</i> = 5.1, 1 H, py), 8.28 (d, <i>J</i> = 3.0, 2 H, aryl), 8.00 (dd, <i>J</i> = 3.0, 9.0, 2 H, aryl), 7.88 (dt, <i>J</i> = 1.5, 7.8, 1 H, py), 7.49 (t, <i>J</i> = 6.0, 1 H, py), 7.19 (d, <i>J</i> = 7.8, 1 H, py), 6.78 (d, <i>J</i> = 9.0, 2 H, aryl), 4.83 (d, <i>J</i> = 14.4, 2 H, C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> ), 4.33 (d, <i>J</i> = 14.4, 2 H, C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> ), 4.24 (s, 2 H, C <sub>5</sub> H <sub>4</sub> CH <sub>2</sub> ) <sup>13</sup> C- <sup>1</sup> H NMR: δ 166.2, 156.2, 150.7, 141.8, 140.7, 126.2, 125.5, 125.0, 124.1, 123.6, 119.5, 60.7, 58.7 IR: ν(WO <sub>2</sub> ) 949s, 914s; ν(NO <sub>2</sub> ) 1510s, 1338s HRMS (LSI): <sup>a</sup> <i>m/z</i> 625.0544 (625.0535)
[WO <sub>2</sub> L <sup>3</sup> ]	57	41.11 (41.47)	2.84 (2.96)	7.05 (7.25)	<sup>1</sup> H NMR: δ 8.97 (d, <i>J</i> = 5.1, 1 H, py), 8.21 (d, <i>J</i> = 3.0, 1 H, aryl), 7.96 (dd, <i>J</i> = 3.0, 9.0, 1 H, aryl), 7.84 (dt, <i>J</i> = 1.5, 7.8, 1 H, py), 7.45 (t, <i>J</i> = 6.3, 1 H, py), 7.25 (dd, <i>J</i> = 1.2, 7.5, 1 H, py), 7.15–7.08 (m, 2 H, aryl), 6.82 (dt, <i>J</i> = 0.9, 7.5, 1 H, aryl), 6.71 (d, <i>J</i> = 9.0, 1 H, aryl), 6.58 (d, <i>J</i> = 7.5, 1 H, aryl), 4.84 (d, <i>J</i> = 13.8, 1 H, aryl CH <sub>2</sub> ), 4.75 (d, <i>J</i> = 13.8, 1 H, aryl CH <sub>2</sub> ), 4.27 (d, <i>J</i> = 14.1, 1 H, aryl CH <sub>2</sub> ), 4.23–4.09 (m, 3 H, aryl CH <sub>2</sub> and C <sub>5</sub> H <sub>4</sub> CH <sub>2</sub> ) <sup>13</sup> C- <sup>1</sup> H NMR: δ 166.8, 160.4, 156.2, 150.5, 141.3, 140.3, 129.9, 129.6, 126.1, 125.5, 124.7, 124.3, 123.4, 122.8, 121.5, 119.4, 118.4, 61.7, 60.7, 58.6 IR: ν(WO <sub>2</sub> ) 944s, 908s; ν(NO <sub>2</sub> ) 1512s, 1339s MS (FAB): a cluster peaking at <i>m/z</i> 590 (69%), [M + H] <sup>+</sup>
[WO <sub>2</sub> L <sup>4</sup> ]	67				<sup>1</sup> H NMR (CDCl <sub>3</sub> ): δ 9.23 (d, <i>J</i> = 4.5, 1 H, py), 8.07 (d, <i>J</i> = 2.7, 1 H, aryl), 7.97 (dd, <i>J</i> = 2.7, 9.0, 1 H, aryl), 7.64 (dt, <i>J</i> = 1.4, 7.7, 1 H, py), 7.30 (t, <i>J</i> = 6.1, 1 H, py), 7.22 (d, <i>J</i> = 2.2, 1 H, aryl), 6.99 (d, <i>J</i> = 2.2, 1 H, aryl), 6.90 (d, <i>J</i> = 7.7, 1 H, py), 6.71 (d, <i>J</i> = 9.0, 1 H, aryl), 5.19–5.09 (m, 2 H, aryl), 4.27 (d, <i>J</i> = 16.5, 1 H, aryl CH <sub>2</sub> ), 4.05–3.91 (m, 3 H, aryl CH <sub>2</sub> and C <sub>5</sub> H <sub>4</sub> CH <sub>2</sub> ), 1.28 (s, 9 H, Bu <sup>t</sup> ), 1.25 (s, 9 H, Bu <sup>t</sup> ) <sup>13</sup> C- <sup>1</sup> H NMR (CDCl <sub>3</sub> ): δ 166.8, 157.0, 155.5, 151.8, 143.9, 140.5, 140.3, 138.7, 125.9, 125.4, 124.6, 124.1, 124.0, 123.0, 121.9, 121.1, 119.8, 63.9, 62.4, 59.3, 34.9, 34.3, 31.5, 29.9 IR: ν(WO <sub>2</sub> ) 946s, 911s; ν(NO <sub>2</sub> ) 1517s, 1338s MS (FAB): a cluster peaking at <i>m/z</i> 691 (100%), [M + H] <sup>+</sup> HRMS (LSI): <sup>a</sup> <i>m/z</i> 692.1769 (692.1936)
[WO <sub>2</sub> L <sup>5</sup> ]	80	41.61 (42.04)	4.25 (4.31)	5.34 (5.45)	<sup>1</sup> H NMR: δ 7.30 (t, <i>J</i> = 8.1, 2 H, aryl), 7.23 (d, <i>J</i> = 7.5, 2 H, aryl), 6.90 (t, <i>J</i> = 7.5, 2 H, aryl), 6.79 (d, <i>J</i> = 8.1, 2 H, aryl), 4.46 (d, <i>J</i> = 14.4, 2 H, C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> ), 4.08 (d, <i>J</i> = 14.4, 2 H, C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> ), 2.76–2.74 (m, 2 H, CH <sub>2</sub> CH <sub>2</sub> ), 2.57 (s, 6 H, CH <sub>3</sub> ), 2.52–2.50 (m, 2 H, CH <sub>2</sub> CH <sub>2</sub> ) <sup>13</sup> C- <sup>1</sup> H NMR: δ 159.4, 129.9, 129.8, 123.8, 121.2, 118.2, 61.6, 57.1, 52.0, 49.7 IR: ν(WO <sub>2</sub> ) 938s, 912s MS (FAB): a cluster peaking at <i>m/z</i> 515 (66%), [M + H] <sup>+</sup>
[WO <sub>2</sub> L <sup>6</sup> ]	65	41.82 (42.04)	4.31 (4.31)	5.34 (5.45)	<sup>1</sup> H NMR: δ 7.28 (t, <i>J</i> = 8.1, 2 H, aryl), 7.15 (d, <i>J</i> = 7.5, 2 H, aryl), 6.90 (t, <i>J</i> = 7.5, 2 H, aryl), 6.79 (d, <i>J</i> = 8.1, 2 H, aryl), 4.73 (d, <i>J</i> = 14.4, 2 H, C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> ), 3.83 (d, <i>J</i> = 14.4, 2 H, C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> ), 2.82 (d, <i>J</i> = 9.6, 2 H, CH <sub>2</sub> CH <sub>2</sub> ), 2.63 (s, 6 H, CH <sub>3</sub> ), 2.43 (d, <i>J</i> = 9.6, 2 H, CH <sub>2</sub> CH <sub>2</sub> ) <sup>13</sup> C- <sup>1</sup> H NMR: δ 157.5, 130.0, 129.5, 122.9, 121.2, 119.0, 63.5, 51.9, 47.6 IR: ν(WO <sub>2</sub> ) 942m, 907s MS (FAB): a cluster peaking at <i>m/z</i> 515 (100%), [M + H] <sup>+</sup>
[WO <sub>2</sub> L <sup>7</sup> ]	43				<sup>1</sup> H NMR: δ 8.21–8.18 (m, 4 H, aryl), 7.03 (d, <i>J</i> = 7.8, 2 H, aryl), 4.74 (d, <i>J</i> = 14.7, 2 H, C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> ), 4.15 (d, <i>J</i> = 14.7, 2 H, C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> ), 2.84 (d, <i>J</i> = 9.6, 2 H, CH <sub>2</sub> CH <sub>2</sub> ), 2.67 (s, 6 H, CH <sub>3</sub> ), 2.54 (d, <i>J</i> = 9.6, 2 H, CH <sub>2</sub> CH <sub>2</sub> ) <sup>13</sup> C- <sup>1</sup> H NMR: δ 163.1, 141.0, 126.4, 125.7, 124.1, 120.2, 62.5, 52.3, 47.8 IR: ν(WO <sub>2</sub> ) 934s, 910s; ν(NO <sub>2</sub> ) 1518s, 1343s MS (FAB): a cluster peaking at <i>m/z</i> 605 (33%), [M + H] <sup>+</sup> HRMS (LSI): <sup>a</sup> <i>m/z</i> 605.0846 (605.0848)
[MoO <sub>2</sub> L <sup>2</sup> ]	90	44.64 (44.79)	2.97 (3.01)	10.54 (10.45)	<sup>1</sup> H NMR: δ 9.01 (d, <i>J</i> = 5.1, 1 H, py), 8.25 (d, <i>J</i> = 3.0, 2 H, aryl), 7.95 (dd, <i>J</i> = 3.0, 9.0, 2 H, aryl), 7.86 (t, <i>J</i> = 7.8, 1 H, py), 7.48 (t, <i>J</i> = 6.4, 1 H, py), 7.19 (d, <i>J</i> = 7.8, 1 H, py), 6.74 (d, <i>J</i> = 9.0, 2 H, aryl), 4.75 (d, <i>J</i> = 14.4, 2 H, C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> ), 4.26 (d, <i>J</i> = 14.4, 2 H, C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> ), 4.11 (s, 2 H, C <sub>5</sub> H <sub>4</sub> CH <sub>2</sub> ) <sup>13</sup> C- <sup>1</sup> H NMR: δ 168.1, 155.2, 150.4, 141.4, 140.4, 126.3, 125.4, 124.9, 124.1, 123.7, 118.8, 60.6, 58.5 IR: ν(MoO <sub>2</sub> ) 918s (br); ν(NO <sub>2</sub> ) 1511s, 1339s HRMS (LSI): <sup>a</sup> <i>m/z</i> 539.0064 (539.0106)
[MoO <sub>2</sub> L <sup>3</sup> ]	87	48.50 (48.89)	3.29 (3.49)	8.35 (8.55)	<sup>1</sup> H NMR: δ 8.99 (d, <i>J</i> = 4.8, 1 H, py), 8.20 (d, <i>J</i> = 2.7, 1 H, aryl), 7.92 (dd, <i>J</i> = 2.7, 9.0, 1 H, aryl), 7.83 (dt, <i>J</i> = 1.5, 7.5, 1 H, py), 7.45 (t, <i>J</i> = 6.3, 1 H, py), 7.25 (dd, <i>J</i> = 1.5, 7.5, 1 H, py), 7.15 (d, <i>J</i> = 7.8, 1 H, aryl), 7.08 (dt, <i>J</i> = 1.5, 7.8, 1 H, aryl), 6.83 (dt, <i>J</i> = 0.9, 7.2, 1 H, aryl), 6.67 (d, <i>J</i> = 9.0, 1 H, aryl), 6.58 (d, <i>J</i> = 7.8, 1 H, aryl), 4.76 (d, <i>J</i> = 14.1, 1 H, aryl CH <sub>2</sub> ), 4.62 (d, <i>J</i> = 14.1, 1 H, aryl CH <sub>2</sub> ), 4.17 (d, <i>J</i> = 14.1, 1 H, aryl CH <sub>2</sub> ), 4.08 (d, <i>J</i> = 14.1, 1 H, aryl CH <sub>2</sub> ), 4.04 (s, 2 H, C <sub>5</sub> H <sub>4</sub> CH <sub>2</sub> ) <sup>13</sup> C- <sup>1</sup> H NMR: δ 168.8, 162.4, 155.3, 150.3, 141.0, 139.8, 130.0, 129.3, 126.2, 125.5, 124.6, 124.3, 123.6, 122.8, 121.4, 118.8, 117.4, 61.4, 60.5, 58.5 IR: ν(MoO <sub>2</sub> ) 944s, 908s; ν(NO <sub>2</sub> ) 1512s, 1339s MS (FAB): a cluster peaking at <i>m/z</i> 494 (17%), [M + H] <sup>+</sup>
[MoO <sub>2</sub> L <sup>4</sup> ]	84				<sup>1</sup> H NMR (CDCl <sub>3</sub> ): δ 9.20 (d, <i>J</i> = 4.9, 1 H, py), 8.06 (d, <i>J</i> = 2.7, 1 H, aryl), 7.94 (dd, <i>J</i> = 2.7, 9.0, 1 H, aryl), 7.63 (dt, <i>J</i> = 1.2, 7.8, 1 H, py), 7.30 (t, <i>J</i> = 6.4, 1 H, py), 7.19 (d, <i>J</i> = 2.3, 1 H, aryl), 6.99 (d, <i>J</i> = 2.3, 1 H, aryl), 6.89 (d, <i>J</i> = 7.8, 1 H, py), 6.68 (d, <i>J</i> = 9.0, 1 H, aryl), 5.01–4.91 (m, 2 H, aryl CH <sub>2</sub> ), 4.13 (d, <i>J</i> = 16.2, 1 H, aryl CH <sub>2</sub> ), 3.92–3.82 (m, 3 H, aryl CH <sub>2</sub> and C <sub>5</sub> H <sub>4</sub> CH <sub>2</sub> ), 1.28 (s, 9 H, Bu <sup>t</sup> ), 1.26 (s, 9 H, Bu <sup>t</sup> ) <sup>13</sup> C- <sup>1</sup> H NMR (CDCl <sub>3</sub> ): δ 168.9, 159.2, 154.7, 151.3, 143.7, 139.9, 137.5, 125.7, 125.5, 124.2, 123.8, 122.9, 122.1, 121.3, 119.2, 63.5, 62.1, 59.1, 35.0, 34.3, 31.5, 29.9 IR: ν(MoO <sub>2</sub> ) 910s (br); ν(NO <sub>2</sub> ) 1510s, 1333s HRMS (LSI): <sup>a</sup> <i>m/z</i> 606.1475 (606.1507)

<sup>a</sup> Calculated values given in parentheses. <sup>b</sup> The NMR spectra were obtained at r.t. in CD<sub>3</sub>SOCD<sub>3</sub> unless otherwise stated; data given as chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (Hz), relative intensity and assignment. The IR spectra (cm<sup>-1</sup>) were recorded as KBr pellets. For high resolution mass spectra the values of *m/z* quoted are based on the most abundant isotope of each element in [M + H]<sup>+</sup>. The bands show the predicted isotopic patterns.

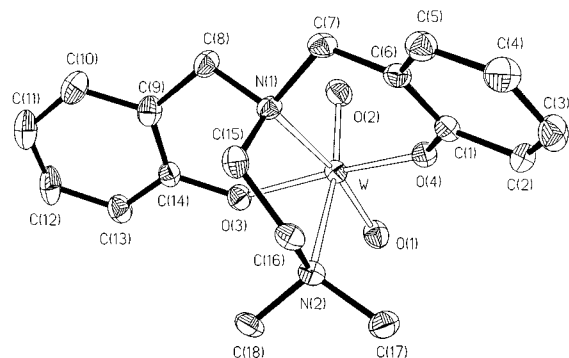
**Table 2** Crystallographic data for  $[\text{WO}_2\text{L}^n]$  ( $n = 1, 5$  or  $6$ ) and  $[\text{MoO}_2\text{L}^2]$ 

	$[\text{WO}_2\text{L}^1]$	$[\text{WO}_2\text{L}^5]$	$[\text{WO}_2\text{L}^6]$	$[\text{MoO}_2\text{L}^2]$
Formula	$\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_4\text{W}$	$\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_4\text{W}$	$\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_4\text{W}$	$\text{C}_{20}\text{H}_{16}\text{MoN}_4\text{O}_8$
Formula weight	534.21	514.23	514.23	536.31
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_12_12_1$ (no. 19)	$C2$ (no. 5)	$P2_1$ (no. 4)
$a/\text{\AA}$	11.7600(11)	11.7880(10)	19.0150(14)	9.4745(4)
$b/\text{\AA}$	14.4350(11)	18.285(2)	7.4238(5)	11.4210(6)
$c/\text{\AA}$	11.8790(11)	8.2640(7)	14.8940(11)	9.5782(4)
$\beta/^\circ$	116.120(4)		119.400(4)	96.172(3)
$U/\text{\AA}^3$	1810.6(3)	1781.3(3)	1831.7(2)	1030.43(8)
$Z$	4	4	4	2
$\mu/\text{mm}^{-1}$	6.409	6.510	6.331	6.695
Unique data measured	2963	3321	2778	3343
Observed data [ $I > 2\sigma(I)$ ], $n$	2804	3261	2671	3267
No. parameters, $p$	317	227	229	299
$R^a$	0.0386	0.0570	0.0539	0.0551
$R^b$	0.0968	0.1421	0.1453	0.1424

<sup>a</sup>  $\Sigma\Delta/\Sigma|F_o|$ . <sup>b</sup>  $[\Sigma w\Delta^2/\Sigma w|F_o|^2]^{1/2}$  where  $\Delta = ||F_o| - |F_c||$ ; weighting scheme,  $w = [\sigma^2(F_o) + 0.009|F_o|^2]^{-1}$ .



**Fig. 1** Molecular structure of  $[\text{WO}_2\text{L}^1]$  showing the atom labelling scheme. Hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 35% probability level.

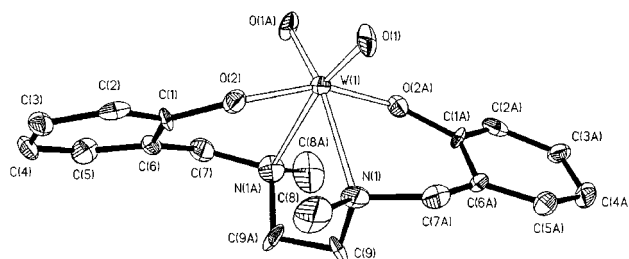


**Fig. 2** Molecular structure of  $[\text{WO}_2\text{L}^5]$ . Details as in Fig. 1.

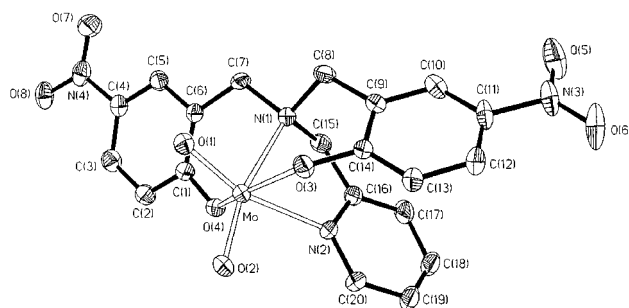
trometry. The FAB or LSI spectra exhibited the corresponding  $[\text{M} + \text{H}]^+$  envelope of which the isotopic distribution was in good agreement with the calculated spectra.

### Structural studies

The structures of four of these complexes, namely  $[\text{WO}_2\text{L}^n]$  ( $n = 1, 5$  or  $6$ ) and  $[\text{MoO}_2\text{L}^2]$ , were established by single crystal X-ray analysis. As shown in Figs. 1–4, all of these compounds exhibit a distorted octahedral geometry with *cis*-dioxo ligands which are *trans* to the two nitrogen atoms of the ligand  $\text{L}^n$ . For  $[\text{WO}_2\text{L}^6]$  an imposed  $C_2$  axis bisects the  $\text{O}(1)\text{--W}(1)\text{--O}(1\text{A})$  angle and two crystallographically independent molecules are present in the unit cell. These tungsten complexes are isostructural with their molybdenum counterparts  $[\text{MoO}_2\text{L}^n]$  ( $n = 1, 5$  or  $6$ ) of which the structures were determined by Spence and



**Fig. 3** Molecular structure of  $[\text{WO}_2\text{L}^6]$ . Details as in Fig. 1.



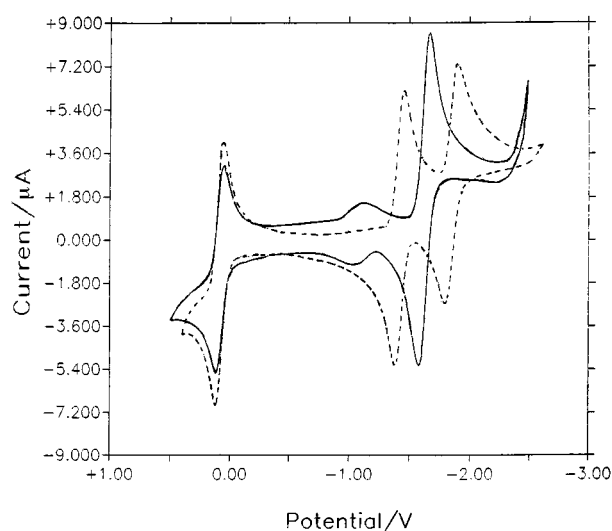
**Fig. 4** Molecular structure of  $[\text{MoO}_2\text{L}^2]$ . Details as in Fig. 1.

co-workers<sup>15</sup> in 1989. Table 3 gives selected bond distances and angles for these complexes. The  $\text{W}=\text{O}$  bond distances (1.719–1.742 Å) are in the range typical of oxotungsten units<sup>30</sup> and are only marginally longer (by 0.02–0.04 Å) than the  $\text{Mo}=\text{O}$  bonds in the respective molybdenum analogues.<sup>15</sup> The  $\text{W}=\text{O}$  single bond distances (1.899–1.952 Å) are comparable with those in other tungsten(vi) alkoxides.<sup>31</sup> The metal–nitrogen bonds are relatively long (>2.30 Å) because of the strong *trans* effect of the oxo ligands. Similar to the molybdenum analogues,<sup>15</sup> the terminal  $\text{W}=\text{N}$  (pyridine) bond in  $[\text{WO}_2\text{L}^1]$  (2.305 Å) is substantially shorter than the terminal  $\text{W}=\text{N}$  (amino) bond in  $[\text{WO}_2\text{L}^5]$  (2.455 Å), while the  $\text{W}=\text{N}$  (tripodal) bond lengths are relatively close in these complexes. The  $\text{N}=\text{W}=\text{N}$  angle is also smaller in  $[\text{WO}_2\text{L}^1]$  than in  $[\text{WO}_2\text{L}^5]$  (71.60 vs. 74.32°). The longer  $\text{W}=\text{N}$  (amino) bond may be attributed to the weaker bonding ( $\text{sp}^3$  vs.  $\text{sp}^2$  N) and the steric effects due to the two methyl groups at nitrogen. Substitution of tungsten for molybdenum has only a small influence on the overall structure. There is no significant difference in metal–ligand bond distances and angles for the isomeric complexes  $[\text{WO}_2\text{L}^5]$  and  $[\text{WO}_2\text{L}^6]$ . The introduction of nitro groups in  $[\text{MoO}_2\text{L}^2]$  does not induce substantial geometrical changes in the structure of the complex as compared with  $[\text{MoO}_2\text{L}^1]$ .<sup>15</sup>

**Table 3** Selected bond distances (Å) and angles (°)<sup>a</sup>

	[WO <sub>2</sub> L <sup>1</sup> ]	[WO <sub>2</sub> L <sup>5</sup> ]	[WO <sub>2</sub> L <sup>6</sup> ]	[MoO <sub>2</sub> L <sup>2</sup> ]
M–O <sub>t</sub> <sup>b</sup>	1.719(2) [O1] 1.734(2) [O4]	1.731(4) [O2] 1.721(3) [O1]	1.723(2) [O1] 1.742(2) <sup>c</sup>	1.7046(11) [O1] 1.7042(13) [O2]
M–O <sub>p</sub> <sup>b</sup>	1.941(2) [O2] 1.943(2) [O3]	1.926(2) [O3] 1.933(3) [O4]	1.952(2) [O2] 1.899(2) <sup>c</sup>	1.9779(13) [O3] 1.9658(11) [O4]
M–N	2.378(2) [N1] 2.305(2) [N2]	2.355(3) [N1] 2.455(4) [N2]	2.403(3) [N1] 2.366(2) <sup>c</sup>	2.384(2) [N1] 2.3157(12) [N2]
O <sub>t</sub> –M–O <sub>t</sub>	107.00(8)	105.8(2)	107.3(2) 108.53(14) <sup>c</sup>	107.70(7)
O <sub>p</sub> –M–O <sub>p</sub>	155.51(7)	158.08(13)	158.3(2) 152.0(2) <sup>c</sup>	154.39(5)
N–M–N	71.60(6)	74.32(12)	75.00(13) 74.81(11) <sup>c</sup>	71.58(5)
O <sub>t</sub> –M–O <sub>p</sub>	98.31(9) [O1, O2] 97.33(9) [O1, O3] 97.67(8) [O4, O2] 95.63(7) [O4, O3]	96.93(13) [O2, O3] 97.98(13) [O2, O4] 95.20(14) [O1, O3] 96.09(13) [O1, O4]	95.75(10) [O1, O2] 97.09(10) [O1, O2A] 95.75(1) <sup>c</sup> 100.48(11) <sup>c</sup>	98.02(6) [O1, O3] 95.99(5) [O1, O4] 99.04(6) [O2, O3] 96.96(6) [O2, O4]
O <sub>t</sub> –M–N	88.54(8) [O1, N1] 160.09(8) [O1, N2] 164.18(6) [O4, N1] 92.91(7) [O4, N2]	89.56(14) [O2, N1] 163.9(2) [O2, N2] 164.6(2) [O1, N1] 90.3(2) [O1, N2]	88.86(10) [O1, N1] 163.80(10) [O1, N1A] 88.46(9) <sup>c</sup> 162.69(9) <sup>c</sup>	89.41(6) [O1, N1] 160.98(6) [O1, N2] 162.46(6) [O2, N1] 91.30(6) [O2, N2]

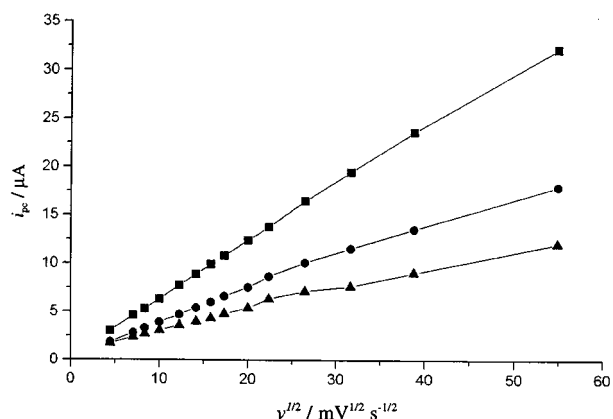
<sup>a</sup> The numbers in parentheses are the estimated standard deviations in the last digit. The atom labels for individual ligand atoms (see Figs. 1–4) appear in square brackets. <sup>b</sup> O<sub>t</sub> = Terminal oxo group, O<sub>p</sub> = phenolic oxygen atom. <sup>c</sup> Data for another crystallographically independent unit.



**Fig. 5** Cyclic voltammograms of [MoO<sub>2</sub>L<sup>1</sup>] (—) and [MoO<sub>2</sub>L<sup>3</sup>] (---) in dmf containing 0.1 mol dm<sup>-3</sup> [NBu<sub>4</sub>][ClO<sub>4</sub>] ( $\nu = 100 \text{ mV s}^{-1}$ ).

### Electrochemical studies

The electrochemical properties of [MO<sub>2</sub>L<sup>n</sup>] (M = Mo or W;  $n = 1-4$ ) were studied by cyclic voltammetry. As shown in Fig. 5, the voltammogram of [MoO<sub>2</sub>L<sup>1</sup>] shows a reduction couple at  $E_2 = -1.61 \text{ V vs. Ag-Ag}^+$  in MeCN together with a weak and broad couple centred at  $-1.09 \text{ V}$ . Ferrocene was also added in all measurements as an internal reference and its oxidation potential ( $E_2 = 0.07 \text{ V vs. Ag-Ag}^+$  in MeCN) remained virtually unchanged. The complexes [MoO<sub>2</sub>L<sup>n</sup>] ( $n = 2-4$ ), which contain one or two nitro groups in the ligands, underwent two reduction processes. The voltammogram of [MoO<sub>2</sub>L<sup>3</sup>] is also given in Fig. 5 for exemplification. The first couple is tentatively assigned to a mainly ligand-based reduction while the second reduction is attributed to the Mo<sup>VI</sup>–Mo<sup>V</sup> couple. The electrochemical data are summarized in Table 4. It can be seen that the first reduction potentials of [MoO<sub>2</sub>L<sup>n</sup>] ( $n = 2-4$ ) are consistent with the electron withdrawing property of the nitro group and the electron donating character of the *tert*-butyl group. This is also observed for the second reduction by considering the half-wave potentials ( $E_2 = -1.835, -1.846$  and  $-1.853 \text{ V}$  for  $n = 2, 3$  and  $4$  respectively) but the effects are less significant. By comparing



**Fig. 6** Plots of  $i_{pc}$  vs.  $\nu^{1/2}$  for [MoO<sub>2</sub>L<sup>4</sup>]: (■) ferrocene, (●) complex 1, (▲) 2.

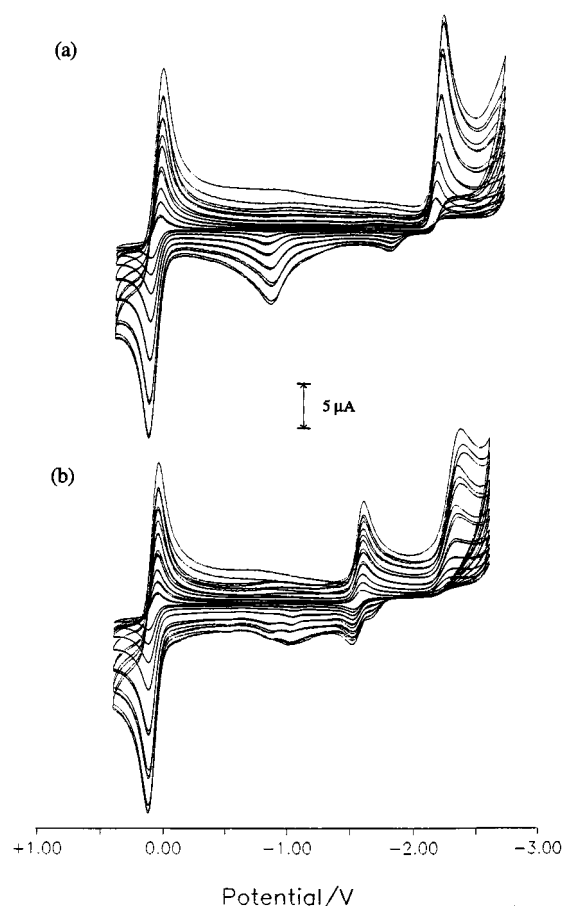
the values of  $\Delta E_p$  of these reduction processes with that of ferrocene which ranges from 64 to 69 mV, these couples are described as quasi-reversible processes. It can be further corroborated by the plots of peak current ( $i_p$ ) vs. square root of the scan rate ( $\nu^{1/2}$ ).<sup>32</sup> A typical plot for [MO<sub>2</sub>L<sup>4</sup>] is shown in Fig. 6 in which a transition clearly occurs at  $\nu^{1/2} \approx 20 \text{ mV}^{1/2} \text{ s}^{-1/2}$  (*i.e.*  $\nu \approx 400 \text{ mV s}^{-1}$ ) for the first and second cathodic peaks characterized as a quasi-reversible process. The plot for ferrocene remains linear throughout the range of scan rates being examined.

The electrochemical behaviour of the tungsten analogues is remarkably different. The voltammogram of [WO<sub>2</sub>L<sup>1</sup>] [Fig. 7(a)] exhibits an irreversible reduction peak at  $-2.16 \text{ V}$  together with two oxidation peaks at  $-1.78$  and  $-0.85 \text{ V}$ . It appears that the latter peaks are due to a species generated from electrochemical reduction of [WO<sub>2</sub>L<sup>1</sup>]. The other tungsten complexes behave similarly except that an extra quasi-reversible couple appears at *ca.*  $-1.6 \text{ V}$  which may be due to the nitro-containing ligand as in the case of the molybdenum analogues. This is exemplified by the voltammogram of [WO<sub>2</sub>L<sup>4</sup>] [Fig. 7(b)] although the two oxidation peaks at  $-1.66$  and  $-1.02 \text{ V}$  are not readily observed in this case. It is worth noting that the metal-based reduction potentials for the tungsten complexes are more negative by 0.34–0.53 V than those of the corresponding molybdenum counterparts and the reductions are less reversible. This is fully consistent with studies of other high valent molybdenum and tungsten complexes.<sup>9a,10d,33</sup>

**Table 4** Electrochemical data for  $[\text{MO}_2\text{L}^n]$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ;  $n = 1-4$ )<sup>a</sup>

Compound	First reduction				Second reduction			
	$E_{\text{pc}}$ (1)	$E_{\text{pa}}$ (1)	$\Delta E_{\text{p}}^b$	$ i_{\text{pa}}/i_{\text{pc}} $	$E_{\text{pc}}$ (2)	$E_{\text{pa}}$ (2)	$\Delta E_{\text{p}}^b$	$ i_{\text{pa}}/i_{\text{pc}} $
$[\text{MoO}_2\text{L}^1]$	-1135	-1036	99	0.43	-1644	-1578	86	0.98
$[\text{MoO}_2\text{L}^2]$	-1277	-1202	75	0.86	-1922	-1748	164	1.12
$[\text{MoO}_2\text{L}^3]$	-1451	-1382	69	0.92	-1898	-1793	105	1.14
$[\text{MoO}_2\text{L}^4]$	-1490	-1412	78	0.87	-1910	-1796	114	1.09
$[\text{WO}_2\text{L}^1]$	—	—	—	—	-2163	—	—	—
$[\text{WO}_2\text{L}^2]$	-1622	-1475	147	0.52	-2450	—	—	—
$[\text{WO}_2\text{L}^3]$	-1587	-1515	62	0.53	-2241	—	—	—
$[\text{WO}_2\text{L}^4]$	-1592	-1520	72	0.46	-2330	—	—	—

<sup>a</sup> Recorded with  $[\text{NBu}_4][\text{ClO}_4]$  as electrolyte in dmf ( $0.1 \text{ mol dm}^{-3}$ ) at ambient temperature. Scan rate =  $100 \text{ mV s}^{-1}$ . Potentials are expressed in mV vs.  $\text{Ag-Ag}^+$  in MeCN. <sup>b</sup>  $\Delta E_{\text{p}} = |E_{\text{pc}} - E_{\text{pa}}|$ .



**Fig. 7** Cyclic voltammograms of (a)  $[\text{WO}_2\text{L}^1]$  and (b)  $[\text{WO}_2\text{L}^4]$  in dmf ( $0.1 \text{ mol dm}^{-3}$   $[\text{NBu}_4][\text{ClO}_4]$ ;  $v$  varies from 20 to  $1000 \text{ mV s}^{-1}$ ).

### Oxo-transfer properties

As the atom transfer chemistry of tungsten is poorly developed,<sup>7,8,9a,f,10d,11,34</sup> the efficacy of these dioxotungsten(vi) complexes to mediate oxo-transfer reactions was examined using benzoin as the reductant and dmsO as the oxo donor. Typically, 0.01 mmol of the complexes  $[\text{WO}_2\text{L}^n]$  ( $n = 1-3, 5$  or  $6$ ) and 25 equivalents of benzoin were dissolved in deoxygenated  $\text{CD}_3\text{SOCD}_3$  ( $0.5 \text{ cm}^3$ ). The mixtures were sealed in NMR tubes and heated at  $100^\circ\text{C}$ . The progress of the reactions was monitored by  $^1\text{H}$  NMR spectrometry which allowed the quantification of benzoin and its oxidized product, benzil as well as the metal complexes. All of these compounds were able to catalyse the oxidation of benzoin by  $\text{CD}_3\text{SOCD}_3$  which proceeded slowly over several days. In a control experiment no reaction between benzoin and  $\text{CD}_3\text{SOCD}_3$  was detected when the complexes were absent. The concentration ratios of  $([\text{benzoin}] + [\text{benzil}])$  to  $[\text{WO}_2\text{L}^n]$  were found to increase gradually during the course of the reactions indicating that part

**Table 5** Percentage conversion of benzoin into benzil<sup>a</sup>

Entry	Catalyst	Conversion (%)
1	$[\text{WO}_2\text{L}^1]$	4
2	$[\text{WO}_2\text{L}^3]$	10
3	$[\text{WO}_2\text{L}^2]$	20
4	$[\text{WO}_2\text{L}^5]$	24
5	$[\text{WO}_2\text{L}^6]$	12
6	$[\text{MoO}_2\text{L}^2]$	65 <sup>b</sup>

<sup>a</sup> Metal complex was treated with 25 equivalents of benzoin in deoxygenated  $\text{CD}_3\text{SOCD}_3$  at  $100^\circ\text{C}$  for 96 h. <sup>b</sup> After 7 h.

of the catalyst was deactivated and consumed. Some unidentified signals also appeared in the  $^1\text{H}$  NMR spectra after prolonged heating which precluded the extraction of kinetic parameters for these catalytic systems. A qualitative comparison of the rate of conversion of benzoin into benzil could however be made. Table 5 shows the percentage conversion of benzoin after heating the mixture at  $100^\circ\text{C}$  for 96 h. It is worth noting that the introduction of the electron withdrawing nitro group facilitates the oxo-transfer process (entries 1-3) and the co-ordination environment of the metal complexes also has substantial effects on the rates of oxo transfers as shown by the data for the structural isomers  $[\text{WO}_2\text{L}^5]$  and  $[\text{WO}_2\text{L}^6]$  (entries 4 and 5). The reactions of these tungsten complexes with benzoin are much slower than the corresponding reactions involving the anionic complexes  $[\text{W}^{\text{VI}}\text{O}_2(\text{bdt})_2]^{2-}$  (bdt = benzene-1,2-dithiolate)<sup>9a,f</sup> and  $[\text{W}^{\text{VI}}\text{O}_2\{\text{O}_2\text{CC}(\text{S})\text{Ph}_2\}]^{2-}$ ,<sup>11</sup> but faster than the reactions involving  $[\text{WO}_2\text{X}(\text{L})]$  [ $\text{L} = \text{hydrotris}(3,5\text{-dimethylpyrazol-1-yl})\text{borate}$ ;  $\text{X} = \text{Oph}$  or  $\text{S}_2\text{PPh}_2\text{-S}$ ], which are inert toward oxygen atom transfer reactions.<sup>10d</sup> For comparison, the oxo-transfer properties of  $[\text{MoO}_2\text{L}^2]$  were also investigated. This molybdenum catalyst was much more efficient in the oxidation of benzoin with dmsO as compared with its tungsten counterpart (entries 6 and 3) which may be rationalized by the difference in reduction potentials ( $-1.92$  vs.  $-2.45 \text{ V}$ ) and  $\text{M}=\text{O}$  bond dissociation energies (*ca.* 410 vs.  $>580 \text{ kJ mol}^{-1}$ ).<sup>7c,10d,30b</sup>

In conclusion, we have synthesized and characterized a series of dioxo-tungsten(vi) and -molybdenum(vi) complexes with tetradentate ligands having an  $\text{N}_2\text{O}_2$  donor set. These compounds can act as catalysts in oxo-transfer reactions although the reactivities appear to be low, in particular for the tungsten complexes which have highly negative reduction potentials and strong  $\text{W}=\text{O}$  bonds.

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