

Synthesis, structure and oxo-transfer properties of dioxotungsten(vi) complexes with pyridine-based *NO*- and *NS*-bidentate ligands

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Treatment of $[\text{WO}_2\text{Cl}_2(\text{DME})]$ with 2-pyridylalkoxo *NO*-bidentate ligands $[\text{HL}^n (n = 1-5)]$ in the presence of *n*-BuLi or 2-pyridylthiolato *NS*-bidentate ligands $[\text{LiL}^n (n = 6, 7)]$ gave the corresponding dioxotungsten(vi) complexes $[\text{WO}_2(\text{L}^n)_2] (n = 1-7)$. The new compounds were spectroscopically characterised and the molecular structures of $[\text{WO}_2(\text{L}^n)_2] (n = 3-5)$ were also determined by X-ray diffraction analysis. While the complexes $[\text{WO}_2(\text{L}^n)_2] (n = 4, 5)$ adopt a normal distorted octahedral geometry with *cis*-dioxo ligands, the metal centre in $[\text{WO}_2(\text{L}^3)_2]$ exhibits an unusual bicapped tetrahedral coordination, which may arise from the strong σ -donating ability of the alkoxo ligands. These high-valent dioxo complexes, in particular $[\text{WO}_2(\text{L}^7)_2]$, which contains two sulfur-containing ligands, are active towards oxygen atom transfer reactions and can catalyse the oxidation of benzoin with DMSO.

High-valent oxotungsten complexes have received considerable attention owing to their usage in various catalytic processes such as alcohol and olefin oxidation,¹ olefin epoxidation² and metathesis reactions.³ Recent findings concerning the biological roles of tungsten have heightened interest in this class of compounds,⁴ in particular those containing dithiolene-type ligands. Due to the structural similarity, this type of ligand serves as an excellent motif to mimic the pterin cofactors in tungsten oxotransferase enzymes.⁵ It is generally believed that most of these organic transformations and biological processes involve oxygen atom transfer reactions as one of the critical steps. Oxo- and dioxotungsten complexes that are able to undergo oxo-transfer reactions are thus of special importance. However, in contrast to the related molybdenum chemistry,⁶ tungsten-mediated atom transfer reactions have been little studied and, to our knowledge, no more than a dozen examples have been reported so far.⁷ We have recently reported several series of dioxotungsten(vi) complexes with N_2O_2 - and N_2S_2 -tetradentate ligands,⁸ N_2O -tridentate ligands⁹ and 2-pyridylamido ligands,¹⁰ using $[\text{WO}_2\text{Cl}_2(\text{DME})]$ as the versatile precursor. It has been found that many of these compounds participate in oxygen atom transfer reactions and can catalyse the oxidation of benzoin with DMSO. As an extension of this work, we report herein a new series of dioxotungsten(vi) complexes with pyridine-based *NO*- and *NS*-bidentate ligands, including their synthesis, structure and oxo-transfer properties.

Experimental

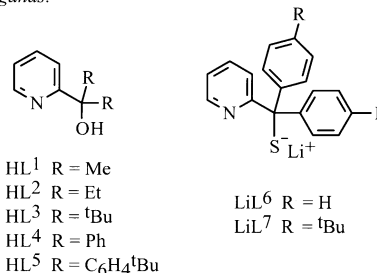
General procedures

All reactions were carried out using standard Schlenk-line techniques under a nitrogen atmosphere. Dichloromethane was dried over 4 Å molecular sieves and distilled from calcium hydride. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium-benzophenone. All other solvents and reagents were of reagent grade and used as received. Chro-

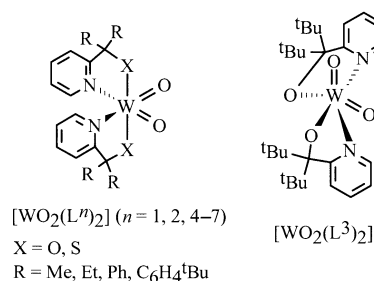
matographic purifications were performed on silica gel columns (Macherey-Nagel, 70–230 mesh) with the indicated eluents. The ligands $\text{HL}^n (n = 2-5,^{11} 6-7^{12})$ and the complex $[\text{WO}_2\text{Cl}_2(\text{DME})]^{13}$ were prepared according to literature procedures.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer (^1H , 300; ^{13}C , 75.4 MHz) in CDCl_3 solutions unless otherwise stated. Chemical shifts were relative to internal SiMe_4 (δ 0). IR spectra were taken on a Nicolet Magna 550 FT-IR spectrometer as KBr pellets. 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 Medac Ltd., Brunel Science Centre, UK.

Ligands:



Complexes:



Preparations

2-(2'-Pyridyl)propan-2-ol(HL¹).¹¹ To a solution of 2-acetylpyridine (1.94 g, 16.0 mmol) in diethyl ether (30 cm³) at 0 °C was added dropwise freshly prepared MeMgI (1.0 M in diethyl ether, 16.0 cm³, 16.0 mmol). A pale yellow solid formed during addition and the mixture was stirred at ambient temperature for 2 h. Water (30 cm³) was then added to the mixture, which was acidified with concentrated HCl until two clear layers were obtained. The aqueous layer was separated and extracted with diethyl ether (3 × 50 cm³). The combined organic portions were dried over anhydrous MgSO₄, concentrated, and chromatographed using hexanes–ethyl acetate (3 : 1) as eluent to give the product as a pale yellow liquid. Yield: 1.36 g (62%). ¹H NMR: δ 8.52 (d, *J* = 4.9, 1 H, H_a), 7.71 (t, *J* = 7.8, 1 H, H_c), 7.39 (d, *J* = 7.8, 1 H, H_d), 7.20 (dd, *J* = 4.9, 7.8 Hz, 1 H, H_b), 5.12 (br s, 1 H, OH), 1.55 (s, 6 H, CH₃). ¹³C{¹H} NMR: δ 165.9, 147.3, 137.0, 121.8, 118.7, 71.6, 30.6.

General procedure for the preparation of [WO₂(Lⁿ)₂] (*n* = 1–5). To a colourless solution of HLⁿ (*n* = 1–5) (2.8–6.0 mmol) in THF (20 cm³) at 0 °C was slowly added a solution of *n*-BuLi in *n*-hexane (1.6 M, 1.1 equiv.). For *n* = 1, 2 and 4, a pale brown precipitate formed immediately. The mixture was stirred at room temperature for 1 h, then a solution of [WO₂Cl₂(DME)] (0.5 equiv.) in THF (20 cm³) was added. The mixture was stirred overnight at room temperature then the volatiles were removed under reduced pressure to give a gray residue that was extracted with CH₂Cl₂ (50–200 cm³). For *n* = 1, 2 and 4, the extract was concentrated to give a solid, which was collected by filtration and washed thoroughly with CHCl₃, diethyl ether and hexanes. The resulting white solid was further purified by recrystallisation from DMF (for *n* = 1 and 4) or CH₂Cl₂ (for *n* = 2). For *n* = 3 and 5, the extract was evaporated and chromatographed using ethyl acetate–ethanol (1 : 1) (for *n* = 3) or CH₂Cl₂ followed with ethyl acetate (for *n* = 5) as eluent. The white solid obtained was then recrystallised from acetone (for *n* = 3) or CHCl₃ (for *n* = 5).

[WO₂(L²)₂]. Yield: 47%. ¹H NMR: δ 8.77 (d, *J* = 5.2, 2 H, H_a), 7.81 (t, *J* = 7.7, 2 H, H_c), 7.26–7.31 (m, 4 H, H_b and H_d), 2.06–2.28 (m, 6 H, CH₂), 1.87 (dq, *J* = 14.5, 7.5, 2 H, CH₂), 1.20 (t, *J* = 7.5, 6 H, CH₃), 0.95 (t, *J* = 7.5 Hz, 6 H, CH₃). ¹³C{¹H} NMR: δ 167.8, 147.4, 138.8, 123.0, 121.0, 90.0, 32.4, 29.9, 8.7, 8.2. IR: ν(WO₂) 931s, 893s cm⁻¹. HRMS (LSI): *m/z* calc. for C₂₀H₂₉N₂O₄W [M + H]⁺ 545.1633, found 545.1693.

[WO₂(L³)₂]. Yield: 83%. ¹H NMR: δ 9.16 (dd, *J* = 1.2, 5.6, 2 H, H_a), 7.81 (dt, *J* = 1.2, 7.9, 2 H, H_c), 7.67 (d, *J* = 7.9, 2 H, H_d), 7.42 (dd, *J* = 5.6, 7.9 Hz, 2 H, H_b), 1.19 (s, 36 H, 'Bu). ¹³C{¹H} NMR: δ 166.0, 148.5, 136.6, 123.2, 122.7, 100.0, 44.7, 29.8. IR: ν(WO₂) 908m, 878s cm⁻¹. HRMS (LSI): *m/z* calc. for C₂₈H₄₅N₂O₄W [M + H]⁺ 657.2888, found 657.2902.

Anal. calc. for C₂₈H₄₄N₂O₄W: C, 51.23; H, 6.76; N, 4.27%. Found: C, 51.11; H, 6.69; N, 4.21%.

[WO₂(L⁴)₂]. Yield: 76%. ¹H NMR: δ 7.58–7.69 (m, 8 H, ArH and PyH), 7.22–7.43 (m, 14 H, ArH and PyH), 7.14 (d, *J* = 7.4, 4 H, ArH), 6.65 (t, *J* = 6.5 Hz, 2 H, PyH). IR: ν(WO₂) 933s, 902s cm⁻¹. HRMS (LSI): *m/z* calc. for C₃₆H₂₉N₂O₄W [M + H]⁺ 737.1637, found 737.1621. Anal. calc. for C₃₆H₂₈N₂O₄W: C, 58.71; H, 3.83; N, 3.80%. Found: C, 58.79; H, 3.81; N, 3.80%.

[WO₂(L⁵)₂]. Yield: 85%. ¹H NMR: δ 7.54–7.62 (m, 8 H, ArH and PyH), 7.29–7.35 (m, 10 H, ArH and PyH), 7.02 (d, *J* = 8.5, 4 H, ArH), 6.55 (t, *J* = 6.4 Hz, 2 H, PyH), 1.38 (s, 18 H, 'Bu), 1.24 (s, 18 H, 'Bu). ¹³C{¹H} NMR: δ 165.3, 151.2, 150.3, 148.4, 144.0, 143.5, 137.9, 128.8, 126.9, 125.0, 124.9, 124.4, 122.3, 94.5, 34.6, 34.4, 31.4, 31.2. IR: ν(WO₂) 936s, 904s cm⁻¹. HRMS (LSI): *m/z* calc. for C₅₂H₆₁N₂O₄W [M + H]⁺ 961.4144, found 961.4271. Anal. calc. for C₅₂H₆₀N₂O₄W: C, 65.00; H, 6.29; N, 2.92%. Found: C, 64.43; H, 6.24; N, 2.52%.

General procedure for the preparation of [WO₂(Lⁿ)₂] (*n* = 6, 7). To a suspension of LiLⁿ (*n* = 6, 7) (4–6 mmol) in THF (50 cm³) was slowly added a solution of [WO₂Cl₂(DME)] (0.5 equiv.) in THF (50–100 cm³) at room temperature. For *n* = 6, a pale yellow solid appeared during addition and the suspension was stirred overnight at room temperature, then filtered. The pale yellow solid obtained was washed thoroughly with THF and dried *in vacuo*. For *n* = 7, the mixture was stirred at room temperature overnight, then evaporated under reduced pressure. The reddish brown residue was extracted with CH₂Cl₂ (50 cm³) and the extract was concentrated and chromatographed using CHCl₃ as eluent to give a pale yellow solid, which was recrystallised from CH₂Cl₂–diethyl ether.

[WO₂(L⁶)₂]. Yield: 85%. IR: ν(WO₂) 940m, 898s cm⁻¹. Anal. calc. for C₃₆H₂₈N₂O₂S₂W: C, 56.26; H, 3.67; N, 3.64; S, 8.34%. Found: C, 56.07; H, 3.99; N, 3.53; S, 7.81%.

[WO₂(L⁷)₂]. Yield: 43%. ¹H NMR (DMSO-*d*₆): δ 9.37 (d, *J* = 4.8, 2 H, H_a), 7.89 (t, *J* = 7.7, 2 H, H_c), 7.34 (d, *J* = 8.7, 4 H, ArH), 7.30 (d, *J* = 8.7, 4 H, ArH), 7.16 (dd, *J* = 4.8, 7.7, 2 H, H_b), 7.10 (d, *J* = 8.7, 4 H, ArH), 6.95 (d, *J* = 8.1, 2 H, H_d), 6.89 (d, *J* = 8.7 Hz, 4 H, ArH), 1.29 (s, 18 H, 'Bu), 1.24 (s, 18 H, 'Bu). ¹³C{¹H} NMR: δ 170.3, 153.4, 150.1, 149.8, 144.3, 144.0, 137.3, 129.2, 128.8, 127.2, 124.8, 124.4, 122.4, 69.2, 34.4 (two overlapping signals), 31.4, 31.3. IR: ν(WO₂) 952m, 908s cm⁻¹. Anal. calc. for C₅₂H₆₀N₂O₂S₂W: C, 62.90; H, 6.09; N, 2.82; S, 6.46%. Found: C, 62.28; H, 5.90; N, 2.76; S, 6.19%.

X-Ray crystallographic analysis of [WO₂(Lⁿ)₂] (*n* = 3–5)

Crystal data and data processing parameters are given in Table 1. Data were collected at 294–296 K on a MSC/Rigaku RAXIS IIC imaging plate system using Mo-Kα radiation (λ = 0.710 73 Å) from a Rigaku RU-200 rotating anode gener-

Table 1 Crystallographic data for [WO₂(Lⁿ)₂] (*n* = 3–5)

	2[WO ₂ (L ³) ₂] · 3H ₂ O	[WO ₂ (L ⁴) ₂] · 2DMF	[WO ₂ (L ⁵) ₂] · 0.5DMF
Formula	C ₅₆ H ₉₄ N ₄ O ₁₁ W ₂	C ₄₂ H ₄₂ N ₄ O ₆ W	C _{53.5} H _{63.5} N _{2.5} O _{4.5} W
Formula weight	1367.05	882.65	997.42
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (no. 14)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 2 ₁ / <i>n</i> (no. 14)
<i>a</i> /Å	20.712(4)	13.467(3)	17.660(3)
<i>b</i> /Å	14.805(3)	24.756(5)	16.118(1)
<i>c</i> /Å	21.362(4)	11.723(2)	19.974(3)
β/°	111.50(3)	100.04(3)	106.760(3)
<i>U</i> /Å ³	6095(2)	3848.5(13)	5444(1)
<i>Z</i>	4	4	4
μ/mm ⁻¹	3.829	3.054	2.164
Reflections collected	9327	6301	7249
Independent reflections	9327	6301	7249
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0468, 0.1264	0.0531, 0.1487	0.0845, 0.1741

ator operating at 50 kV and 90 mA.¹⁴ A self-consistent semi-empirical absorption correction based on Fourier coefficient fitting of symmetry-equivalent reflections was applied by using the ABCOR program.¹⁵ The structures were solved by direct methods, which yielded the positions of all non-hydrogen atoms, which were refined anisotropically. Hydrogen atoms were placed in their idealised 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 the SHELXTL program package (PC version).¹⁶

CCDC reference number 440/236. See <http://www.rsc.org/suppdata/nj/b0/b006979p/> for crystallographic files in .cif format.

Results and discussion

Synthesis and spectroscopic characterisation

The pyridine-based *NO*-bidentate ligands HL^n ($n = 2-5$) were prepared by lithiation of 2-bromopyridine, followed by treatment with the corresponding ketones.¹¹ As the reaction of the lithiated pyridine with acetone only gave HL^1 in low yield, this ligand was prepared with an alternative pathway that involved the reaction of 2-acetylpyridine with $MeMgI$. The *NS*-bidentate ligands LiL^n ($n = 6, 7$) were synthesised according to the method described by Holm and co-workers.¹² Starting from the respective 2-diarylmethylpyridine, lithiation followed by the addition of elemental sulfur afforded these ligands in good yield.

Reaction of $[WO_2Cl_2(DME)]$ with 2 equiv. of these ligands in the presence of *n*-BuLi [for HL^n ($n = 1-5$)] yielded the corresponding dioxotungsten(vi) complexes $[WO_2(L^n)_2]$ ($n = 1-7$) in 43–85% yield. The DME complex has proven to be a versatile precursor of a wide range of dioxotungsten(vi) complexes due to its ease of preparation, high solubility in common organic solvents and high reactivity towards ligand substitution reactions.^{8-10,17} During the course of this study, Herrmann and co-workers have reported the preparation and structure of $[WO_2(L^1)_2]$ using WO_2Cl_2 and $WO_2(acac)_2$ as the starting materials.^{2c}

All the dioxo complexes are stable to air and moisture. With the exception of $[WO_2(L^6)_2]$, which is virtually insoluble in most organic solvents, all complexes were characterised with elemental analysis {except $[WO_2(L^2)_2]$ } and a range of spectroscopic methods. The NMR data were in accord with the proposed structures shown. This can be well illustrated by the 1H NMR spectra of $[WO_2(L^n)_2]$ ($n = 5, 7$), which show two singlets for the *tert*-butyl groups, indicating the presence of an internal C_2 rotation axis. The IR spectra of all these dioxo complexes exhibit two medium to strong bands within the 878–908 and 908–952 cm^{-1} ranges, attributable to the asymmetric and symmetric W=O stretches, respectively, in a *cis*-dioxo moiety.¹⁸ The LSI mass spectra of $[WO_2(L^n)_2]$ ($n = 2-5$) were also recorded and show the corresponding $[M + H]^+$ envelope with the expected isotopic pattern.

Structural studies

The structures of three of these complexes, namely $[WO_2(L^n)_2]$ ($n = 3-5$), were established by single-crystal X-ray analysis. Fig. 1 and 2 display the molecular structures of $[WO_2(L^4)_2]$ and $[WO_2(L^5)_2]$, respectively, which are isostructural with their molybdenum counterparts.¹² Like many other dioxomolybdenum(vi) and dioxotungsten(vi) complexes with nitrogen-donor-containing bi- and tetradentate ligands,^{2c,8,12,19} these compounds adopt a distorted octahedral geometry with the N atoms *trans* to the terminal oxo groups. Due in part to the Coulombic repulsion between the

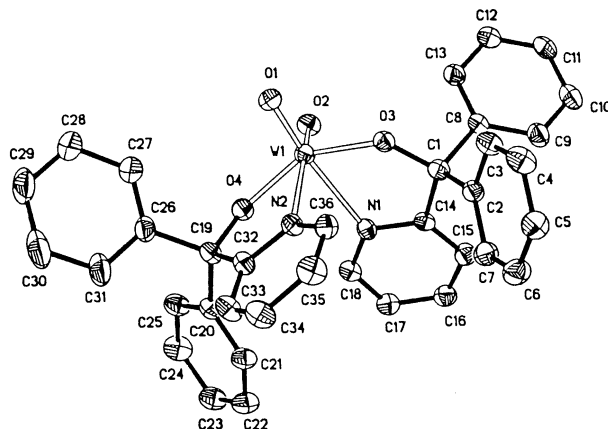


Table 2 Selected bond distances (Å) and angles (°)^a in [WO₂(Lⁿ)₂] (*n* = 3–5)

	[WO ₂ (L ³) ₂]	[WO ₂ (L ⁴) ₂]	[WO ₂ (L ⁵) ₂]
W–O _t ^b	1.756(2), 1.7474(19) ^c [O2] 1.7498(18), 1.7363(18) ^c [O4]	1.731(2) [O1] 1.733(2) [O2]	1.725(3) [O2] 1.695(3) [O3]
W–O _a ^b	1.9147(17), 1.9281(17) ^c [O1] 1.9129(16), 1.9253(17) ^c [O3]	1.938(2) [O3] 1.930(2) [O4]	1.952(3) [O1] 1.933(3) [O4]
W–N	2.2873(18), 2.3013(18) ^c [N1] 2.3098(19), 2.3040(19) ^c [N2]	2.341(3) [N1] 2.357(2) [N2]	2.343(4) [N1] 2.322(3) [N2]
O _t –W–O _t	115.69(9), 113.76(9) ^c	105.35(10)	107.41(14)
O _a –W–O _a	78.73(6), 77.37(7) ^c	149.16(8)	150.66(12)
N–W–N	142.13(7), 145.84(8) ^c	81.98(8)	80.49(11)
O _t –W–O _a	117.01(8), 122.07(8) ^c [O2, O1] 112.44(7), 107.71(8) ^c [O2, O3] 111.49(8), 109.46(8) ^c [O4, O1] 116.34(8), 122.50(7) ^c [O4, O3] ^c	93.57(9) [O1, O3] 104.78(9) [O1, O4] 104.88(8) [O2, O3] 94.05(8) [O2, O4]	103.19(15) [O2, O1] 95.27(15) [O2, O4] 92.39(14) [O3, O1] 103.72(14) [O3, O4]
O _t –W–N	78.62(8), 80.46(8) ^c [O2, N1] 81.06(8), 82.15(8) ^c [O2, N2] 81.17(8), 81.62(7) ^c [O4, N1] 79.36(7), 78.85(8) ^c [O4, N2]	162.45(8) [O1, N1] 86.85(9) [O1, N2] 88.40(9) [O2, N1] 163.72(8) [O2, N2]	85.96(13) [O2, N1] 161.72(14) [O2, N2] 161.57(15) [O3, N1] 88.70(13) [O3, N2]
O _a –W–N	69.88(7), 69.59(7) ^c [O1, N1] 147.88(7), 143.80(7) ^c [O1, N2] 148.16(7), 144.54(7) ^c [O3, N1] 69.58(7), 69.15(8) ^c [O3, N2]	72.02(8) [O3, N1] 84.66(7) [O3, N2] 84.65(8) [O4, N1] 72.08(7) [O4, N2]	71.81(13) [O1, N1] 84.23(13) [O1, N2] 87.18(13) [O4, N1] 71.98(13) [O4, N2]

^a The numbers in parentheses are the estimated standard deviations in the last digit. The atom labels for individual ligand atoms (see Fig. 1–3) appear in brackets. ^b O_t = terminal oxo group; O_a = alkoxo oxygen atom. ^c Data for another crystallographically independent unit.

Oxo-transfer properties

The oxygen atom transfer behaviour of [WO₂(Lⁿ)₂] (*n* = 1, 3, 5, 7) was examined using benzoin as the reductant and DMSO

as the oxo donor as described before.⁸ Typically, 0.01 mmol of the complex and 25 equiv. of benzoin were dissolved in deoxygenated DMSO-d₆ (0.5 cm³). The mixtures were sealed in NMR tubes and heated at 80–100 °C. All these complexes were able to catalyse the oxidation of benzoin to benzil with DMSO and the progress of the reactions was followed by ¹H NMR spectroscopy. It was found that the concentration ratios of ([benzoin] + [benzil]) to [WO₂(Lⁿ)₂] increased gradually during the course of the reactions, showing that part of the catalyst was deactivated and consumed. Some unidentified signals were also observed in the ¹H NMR spectra after prolonged heating, which precluded a detailed kinetic analysis. A qualitative comparison could, however, be made. Table 3 shows the percentage conversion of benzoin to benzil using [WO₂(Lⁿ)₂] (*n* = 1, 3, 5, 7) as the catalysts. The values are comparable with those of dioxotungsten(vi) complexes with analogous tetradentate ligands.⁸ The complex having two NS-bidentate ligands, [WO₂(L⁷)₂], shows the best performance in this series of complexes, giving a higher percentage conversion within a shorter reaction time, even at a lower temperature (80 °C). These results clearly indicate that thiolato ligands have substantial effects in promoting the oxo-transfer reactivity of this class of oxo complexes.^{8b} The efficacy of [WO₂(L⁷)₂] towards oxo-transfer, however, is still lower than that of analogous molybdenum complexes⁸ and the related [WO₂(bdt)₂]^{2–} (bdt = benzene-1,2-dithiolate)^{5a,22} and [WO₂{O₂CC(S)Ph₂}]^{2–} complexes.²³

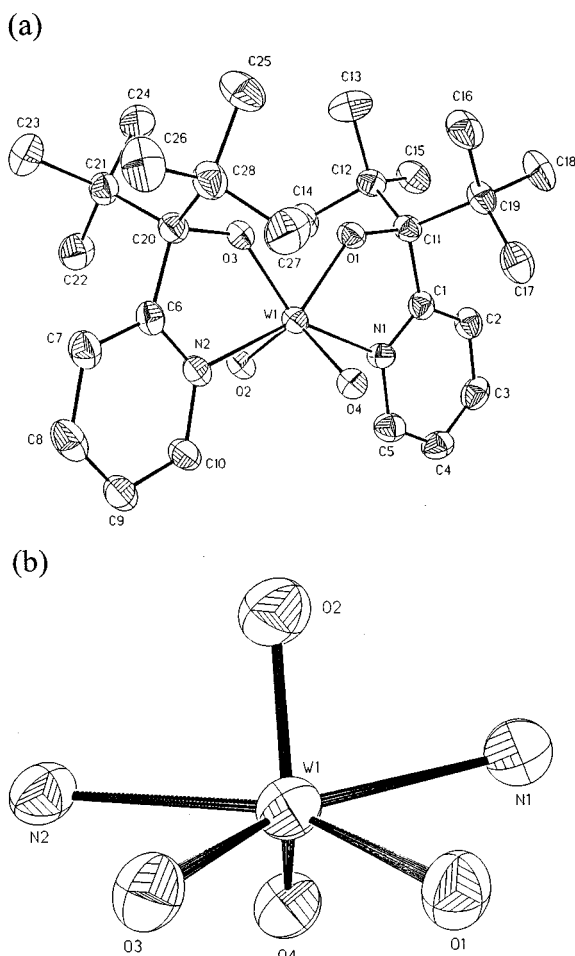


Fig. 3 (a) Molecular structure and atom labelling scheme for [WO₂(L³)₂]. Hydrogen atoms are omitted for clarity. (b) An expanded view of the tungsten coordination sphere.

Table 3 Percentage conversion of benzoin into benzil^a using [WO₂(Lⁿ)₂] as catalyst

Entry	Catalyst	<i>T</i> /°C	<i>t</i> /h	Conv. (%)
1	[WO ₂ (L ¹) ₂]	100	96	13
2	[WO ₂ (L ³) ₂]	100	96	15
3	[WO ₂ (L ⁵) ₂]	100	96	26
4	[WO ₂ (L ⁷) ₂]	100	7	37
5	[WO ₂ (L ⁷) ₂]	100	48	83
6	[WO ₂ (L ⁷) ₂]	80	48	52
7	[WO ₂ (L ⁷) ₂]	80	96	76

^a Metal complex was treated with 25 equiv. of benzoin in deoxygenated DMSO-d₆.

In summary, we have prepared and characterised, both spectroscopically and structurally, a series of dioxotungsten(vi) complexes with pyridine-based *NO*- and *NS*-bidentate ligands that possess different steric and electronic properties. These high-valent species exhibit tungsten-mediated oxo-transfer activity, which has been little studied so far. It can be envisaged that the reactivity towards oxo-transfer reactions can be optimised by rational modification of the ligands, which may lead to more efficient tungsten-based oxidation catalysts. This work is still in progress.

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