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

Yee-Lok Wong, Qingchuan Yang, Zhong-Yuan Zhou, Hung Kay Lee, Thomas C. W. Mak and Dennis K. P. Ng*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N. T., Hong Kong, China. E-mail: dkpn@cuhk.edu.hk

Received (in Montpellier, France) 28th August 2000, Accepted 26th October 2000 First published as an Advance Article on the web 22nd December 2000

Treatment of $[WO_2Cl_2(DME)]$ with 2-pyridylalkoxo NO-bidentate ligands $[HL^n (n = 1-5)]$ in the presence of *n*-BuLi or 2-pyridylthiolato NS-bidentate ligands $[LiL^n (n = 6, 7)]$ gave the corresponding dioxotungsten(v1) complexes $[WO_2(L^n)_2] (n = 1-7)$. The new compounds were spectroscopically characterised and the molecular structures of $[WO_2(L^n)_2] (n = 3-5)$ were also determined by X-ray diffraction analysis. While the complexes $[WO_2(L^n)_2] (n = 4, 5)$ adopt a normal distorted octahedral geometry with *cis*-dioxo ligands, the metal centre in $[WO_2(L^3)_2]$ 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 $[WO_2(L^7)_2]$, 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_2 -tridentate ligands,⁹ and 2-pyridylamido ligands,¹⁰ using $[WO_2Cl_2(DME)]$ 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. Chromatographic purifications were performed on silica gel columns (Macherey–Nagel, 70–230 mesh) with the indicated eluents. The ligands HL^n (n = 2-5,¹¹ 6–7¹²) and the complex [WO₂Cl₂(DME)]¹³ were prepared according to literature procedures.

The ¹H and ¹³C NMR spectra were recorded on a Bruker DPX 300 spectrometer (¹H, 300; ¹³C, 75.4 MHz) in CDCl₃ solutions unless otherwise stated. Chemical shifts were relative to internal SiMe₄ (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.



DOI: 10.1039/b006979p

New J. Chem., 2001, 25, 353–357 353

2-(2'-Pyridyl)propan-2-ol(HL1).11 To a solution of 2acetylpyridine (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 $(3 \times 50 \text{ cm}^3)$. 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 $[WO_2(L^n)_2]$ (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 $[WO_2Cl_2(DME)]$ (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 CH_2Cl_2 (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).

 $\begin{bmatrix} WO_2(L^2)_2 \end{bmatrix}. \text{ Yield: } 47\%. \ ^1\text{H NMR: } \delta 8.77 \text{ (d, } J = 5.2, 2 \text{ H,} \\ \text{H}_a \end{bmatrix}, 7.81 \text{ (t, } J = 7.7, 2 \text{ H, } \text{H}_c), 7.26-7.31 \text{ (m, 4 H, } \text{H}_b \text{ and } \text{H}_d), \\ 2.06-2.28 \text{ (m, 6 H, CH}_2), 1.87 \text{ (dq, } J = 14.5, 7.5, 2 \text{ H, CH}_2), \\ 1.20 \text{ (t, } J = 7.5, 6 \text{ H, CH}_3), 0.95 \text{ (t, } J = 7.5 \text{ Hz, 6 H, CH}_3). \\ ^{13}\text{C}\{^1\text{H}\} \text{ NMR: } \delta 167.8, 147.4, 138.8, 123.0, 121.0, 90.0, 32.4, \\ 29.9, 8.7, 8.2. \text{ IR: } v(WO_2) 931\text{s}, 893\text{s cm}^{-1}. \text{ HRMS (LSI): } m/z \\ \text{calc. for } \text{C}_{20}\text{H}_{29}\text{N}_2\text{O}_4\text{W} \text{ [M + H]}^+ 545.1633, \text{ found } 545.1693. \\ \end{bmatrix}$

 $[WO_2(L^3)_2]$. 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, ¹Bu). 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.

Table 1 Crystallographic data for $[WO_2(L^n)_2]$ (n = 3-5)

Anal. calc. for $C_{28}H_{44}N_2O_4W$: C, 51.23; H, 6.76; N, 4.27%. Found: C, 51.11; H, 6.69; N, 4.21%.

 $[WO_2(L^4)_2]$. 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: $v(WO_2)$ 933s, 902s cm⁻¹. HRMS (LSI): m/z calc. for $C_{36}H_{29}N_2O_4W$ [M + H]⁺ 737.1637, found 737.1621. Anal. calc. for $C_{36}H_{28}N_2O_4W$: C, 58.71; H, 3.83; N, 3.80%. Found: C, 58.79; H, 3.81; N, 3.80%.

 $[WO_2(L^5)_2]$. 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: $v(WO_2)$ 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 $[WO_2(L^n)_2]$ (n = 6,7). To a suspension of LiLⁿ (n = 6, 7) (4-6 mmol) in THF (50 cm³) was slowly added a solution of $[WO_2Cl_2(DME)]$ (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.

 $[WO_2(L^6)_2]$. Yield: 85%. IR: $v(WO_2)$ 940m, 898s cm⁻¹. Anal. calc. for $C_{36}H_{28}N_2O_2S_2W$: 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%.

 $[WO_2(L^7)_2]$. Yield: 43%. ¹H NMR (DMSO-d₆): 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 $[WO_2(L^n)_2]$ (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-K α radiation ($\lambda = 0.71073$ Å) from a Rigaku RU-200 rotating anode gener-

	$2[WO_2(L^3)_2] \cdot 3H_2O$	$[WO_2(L^4)_2] \cdot 2DMF$	$[WO_2(L^5)_2] \cdot 0.5DMF$
Formula Formula weight Crystal system Space group a/Å b/Å c/Å $\beta/^{\circ}$ $U/Å^{3}$ Z μ/m^{-1} Reflections collected	$\begin{array}{c} C_{56}H_{94}N_4O_{11}W_2\\ 1367.05\\ Monoclinic\\ P2_1/n (no. 14)\\ 20.712(4)\\ 14.805(3)\\ 21.362(4)\\ 111.50(3)\\ 6095(2)\\ 4\\ 3.829\\ 9337\\ \end{array}$	$\begin{array}{c} C_{42}H_{42}N_4O_6W\\ 882.65\\ Monoclinic\\ P2_1/c (no. 14)\\ 13.467(3)\\ 24.756(5)\\ 11.723(2)\\ 100.04(3)\\ 3848.5(13)\\ 4\\ 3.054\\ 6301\end{array}$	$\begin{array}{c} C_{53.5}H_{63.5}N_{2.5}O_{4.5}W\\ 997.42\\ Monoclinic\\ P2_1/n (no. 14)\\ 17.660(3)\\ 16.118(1)\\ 19.974(3)\\ 106.760(3)\\ 5444(1)\\ 4\\ 2.164\\ 7249\end{array}$
Independent reflections Final R_1 , wR_2 [$I > 2\sigma(I)$]	9327 9327 0.0468, 0.1264	6301 0.0531, 0.1487	7249 7249 0.0845, 0.1741

ator operating at 50 kV and 90 mA.¹⁴ A self-consistent semiempirical absorption correction based on Fourier coefficient fitting of symmetry-equivalent reflections was applied by using the ABSCOR 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 LiLⁿ (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 HLⁿ (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



Fig. 1 Molecular structure and atom labelling scheme for $[WO_2(L^4)_2]$. Hydrogen atoms are omitted for clarity.

terminal oxo (O_t) and alkoxo (O_a) oxygen atoms, the O_a-W-O_a angles [149.16(8)-150.66(12)°] deviate substantially from the idealised 180° value. Table 2 summarises selected bond lengths and angles of these two complexes, which are unexceptional.

In contrast, the structure of $[WO_2(L^3)_2]$ is remarkably different. Two crystallographically independent molecules were revealed in the unit cell, one of which is shown in Fig. 3(a). The structure can be described as a bicapped tetrahedron in which the four oxygen atoms form the distorted tetrahedron and the two nitrogen atoms occupy the capping positions [Fig. 3(b)]. This unusual nonoctahedral geometry is similar to that of $[MoO_2(SCMe_2CR_2NHR)_2]$ (R = H, Me), which was described as a skew trapezoidal bipyramid by Stiefel and coworkers, with the oxo groups at the apices and the trapezoidal plane defined by the two S and two N atoms of the two bidentate ligands.²⁰ It is likely that due to the strong electronreleasing ability of the tert-butyl groups, the alkoxo ligands in $[WO_2(L^3)_2]$ become very strong σ donors, which interact strongly with the metal centre and push the pyridyl ligands to the capping positions. The strong σ -donating ability also prevents the two alkoxo ligands from occupying an opposite position or trans to the oxo groups, resulting in the formation of this unusual structure. Apart from this electronic factor, steric influence arising from the bulky tert-butyl groups may also play a significant role. As shown in Table 2, the W=O bonds in $[WO_2(L^3)_2]$ are slightly longer than those in $[WO_2(L^n)_2]$ (n = 4, 5) by ca. 0.03 Å, while the W–O and W–N single bonds are slightly shorter by ca. 0.02 and 0.04 Å, respectively, due to the stronger σ -donating alkoxo ligands and the absence of trans influence arising from the oxo groups.18b,21



Fig. 2 Molecular structure and atom labelling scheme for $[WO_2(L^5)_2]$. Hydrogen atoms are omitted for clarity.

Table 2 Selected bond distances (Å) and angles $(^{\circ})^a$ in $[WO_2(L^n)_2]$ (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)° [N1] 2.3098(19), 2.3040(19)° [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)
$\dot{O_a} - W - \dot{O_a}$	$78.73(6), 77.37(7)^{c}$	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]	93.57(9) [O1, O3]	103.19(15) [O2, O1]
-	112.44(7), 107.71(8) ^c [O2, O3]	104.78(9) [O1, O4]	95.27(15) [O2, O4]
	111.49(8), 109.46(8) ^c [O4, O1]	104.88(8) [O2, O3]	92.39(14) [O3, O1]
	116.34(8), 122.50(7) [O4, O3] ^c	94.05(8) [O2, O4]	103.72(14) [O3, O4]
O _t -W-N	78.62(8), 80.46(8) ^c [O2, N1]	162.45(8) [O1, N1]	85.96(13) [O2, N1]
	81.06(8), 82.15(8) ^c [O2, N2]	86.85(9) [O1, N2]	161.72(14) [O2, N2]
	81.17(8), 81.62(7) ^c [O4, N1]	88.40(9) [O2, N1]	161.57(15) [O3, N1]
	79.36(7), 78.85(8) ^c [O4, N2]	163.72(8) [O2, N2]	88.70(13) [O3, N2]
O _a –W–N	69.88(7), 69.59(7) ^c [O1, N1]	72.02(8) [O3, N1]	71.81(13) [O1, N1]
	147.88(7), 143.80(7) ^c [O1, N2]	84.66(7) [O3, N2]	84.23(13) [O1, N2]
	148.16(7), 144.54(7) ^c [O3, N1]	84.65(8) [O4, N1]	87.18(13) [O4, N1]
	69.58(7), 69.15(8) ^c [O3, N2]	72.08(7) [O4, N2]	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 $[WO_2(L^n)_2]$ (n = 1, 3, 5, 7) was examined using benzoin as the reductant and DMSO



Fig. 3 (a) Molecular structure and atom labelling scheme for $[WO_2(L^3)_2]$. Hydrogen atoms are omitted for clarity. (b) An expanded view of the tungsten coordination sphere.

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 $[WO_2(L^n)_2]$ 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 $[WO_2(L^n)_2]$ (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 NSbidentate ligands, $[WO_2(L^7)_2]$, 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 $[WO_2(L^7)_2]$ towards oxo-transfer, however, is still lower than that of analogous molybdenum complexes⁸ and the related $[WO_2(bdt)_2]^{2^-} (bdt = benzene-1,2-dithiolate)^{5a,22}$ $[WO_2\{O_2CC(S)Ph_2\}]^{2^-} complexes.^{23}$ and

Table 3 Percentage conversion of benzoin into benzil^{*a*} using $[WO_2(L^n)_2]$ as catalyst

Entry	Catalyst	$T/^{\circ}\mathbf{C}$	t/h	Conv. (%)
1	$[WO_2(L^1)_2]$	100	96	13
2	$\left[WO_2(L^3)_2 \right]$	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-d $_6$. In summary, we have prepared and characterised, both spectroscopically and structurally, a series of dioxotungsten(v_I) complexes with pyridine-based *NO*- and *NS*bidentate ligands that possess different steric and electronic properties. These high-valent species exhibit tungstenmediated oxo-transfer activity, which has been little studied so far. It can be envisaged that the reactivity towards oxotransfer 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.

Acknowledgements

We thank Prof. Zhenyang Lin for helpful discussion and the Research Grants Council of the Hong Kong Special Administrative Region, China (Earmarked Grant: CUHK 464/95P) for financial support.

References

- R. A. Sheldon and J. K. Kochi, *Metal-catalyzed Oxidation of* Organic Compounds, Academic Press, New York, 1981; K. Sato, M. Aoki and R. Noyori, Science, 1998, **281**, 1646; K. Sato, M. Aoki, J. Takagi, K. Zimmermann and R. Noyori, Bull. Chem. Soc. Jpn., 1999, **72**, 2287.
- 2 (a) K. Sato, M. Aoki, M. Ogawa, T. Hashimoto and R. Noyori, J. Org. Chem., 1996, 61, 8310; (b) K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, D. Panyella and R. Noyori, Bull. Chem. Soc. Jpn., 1997, 70, 905; (c) W. A. Herrmann, J. Fridgen, G. M. Lobmaier and M. Spiegler, New J. Chem., 1999, 23, 5; (d) W. A. Herrmann, J. J. Haider, J. Fridgen, G. M. Lobmaier and M. Spiegler, J. Organomet. Chem., 2000, 603, 69.
- 3 K. J. Ivin and J. C. Mol, Olefin Metathesis and Metathesis Polymerization, Academic Press, San Diego, 1997; Y. Nakayama, N. Ikushima and A. Nakamura, Chem. Lett., 1997, 861; Y. Nakayama, N. Ikushima, N. Ueyama, A. Nakamura and A. Harada, Chem. Lett., 2000, 434.
- 4 M. J. Johnson, D. C. Rees and M. W. W. Adams, Chem. Rev., 1996, 96, 2817; W. R. Hagen and A. F. Arendsen, Struct. Bond., 1998, 90, 161.
- 5 See, for example: (a) N. Ueyama, H. Oku and A. Nakamura, J. Am. Chem. Soc., 1992, 114, 7310; (b) S. K. Das, D. Biswas, R. Maiti and S. Sarkar, J. Am. Chem. Soc., 1996, 118, 1387; (c) E. S. Davies, G. M. Aston, R. L. Beddoes, D. Collison, A. Dinsmore, A. Docrat, J. J. Joule, C. R. Wilson and C. D. Garner, J. Chem. Soc., Dalton Trans., 1998, 3647; (d) K.-M. Sung and R. H. Holm, Inorg. Chem., 2000, 39, 1275 and references therein.

- R. H. Holm, Coord. Chem. Rev., 1990, 100, 183; R. H. Holm and J. P. Donahue, Polyhedron, 1993, 12, 571; H. Arzoumanian, Coord. Chem. Rev., 1998, 178–180, 191; C. G. Young, in Biomimetic Oxidations Catalyzed by Transition Metal Complexes, ed. B. Meunier, Imperial College Press, London, 2000, ch. 9.
- G. C. Tucci, J. P. Donahue and R. H. Holm, *Inorg. Chem.*, 1998, 37, 1602 and references therein.
- 8 (a) Y.-L. Wong, Y. Yan, E. S. H. Chan, Q. Yang, T. C. W. Mak and D. K. P. Ng, J. Chem. Soc., Dalton Trans., 1998, 3057; (b) Y.-L. Wong, J.-F. Ma, W.-F. Law, Y. Yan, W.-T. Wong, Z.-Y. Zhang, T. C. W. Mak and D. K. P. Ng, Eur. J. Inorg. Chem., 1999, 313.
- 9 Y.-L. Wong, J.-F. Ma, F. Xue, T. C. W. Mak and D. K. P. Ng, Organometallics, 1999, 18, 5075.
- 10 H. K. Lee, Y.-L. Wong, Z.-Y. Zhou, Z.-Y. Zhang, D. K. P. Ng and T. C. W. Mak, J. Chem. Soc., Dalton Trans., 2000, 539.
- 11 W. A. Herrmann, G. M. Lobmaier, T. Priermeier, M. R. Mattner and B. Scharbert, J. Mol. Catal. A, 1997, 117, 455.
- 12 B. E. Schultz, S. F. Gheller, M. C. Muetterties, M. J. Scott and R. H. Holm, J. Am. Chem. Soc., 1993, 115, 2714.
- 13 K. Dreisch, C. Andersson and C. Stålhandske, *Polyhedron*, 1991, 10, 2417.
- 14 J. Tanner and K. Krause, *Rigaku J.*, 1994, **11**, 4; J. Tanner and K. Krause, *Rigaku J.*, 1990, **7**, 28; K. L. Krause and G. N. Phillips, Jr., J. Appl. Crystallogr., 1992, **25**, 146; M. Sato, M. Yamamoto, K. Imada, Y. Katsube, N. Tanaka and T. Higashi, J. Appl. Crystallogr., 1992, **25**, 348.
- 15 T. Higashi, ABSCOR, An empirical absorption correction based on Fourier coefficient fitting, Rigaku Corporation, Tokyo, 1995.
- 16 SHELXTL PC v5.0 Reference Manual, Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1995.
- K. Dreisch, C. Andersson and C. Stålhandske, *Polyhedron*, 1992, 11, 2143; K. Dreisch, C. Andersson and C. Stålhandske, *Polyhedron*, 1993, 12, 303 and 1335; K. Dreisch, C. Andersson, M. Håkansson and S. Jagner, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 1045.
- 18 (a) H. Oku, N. Ueyama and A. Nakamura, *Inorg. Chem.*, 1995, 34, 3667; (b) A. A. Eagle, E. R. T. Tiekink and C. G. Young, *Inorg. Chem.*, 1997, 36, 6315.
- A. Bruce, J. L. Corbin, P. L. Dahlstrom, J. R. Hyde, M. Minelli, E. I. Stiefel, J. T. Spence and J. Zubieta, *Inorg. Chem.*, 1982, 21, 917; P. Subramanian, J. T. Spence, R. Ortega and J. H. Enemark, *Inorg. Chem.*, 1984, 23, 2564; U. Küsthardt, R. W. Albach and P. Kiprof, *Inorg. Chem.*, 1993, 32, 1838; S. Shanmuga, S. Raj, H.-K. Fun, Z.-F. Chen, J. Zhang, X. Xue, R.-G. Xiong and X.-Z. You, *Acta Crystallogr.*, Sect. C, 1999, 55, 2037.
- 20 J. M. Berg, D. J. Spira, K. O. Hodgson, A. E. Bruce, K. F. Miller, J. L. Corbin and E. I. Stiefel, *Inorg. Chem.*, 1984, 23, 3412.
- 21 A. A. Eagle, G. N. George, E. R. T. Tiekink and C. G. Young, *Inorg. Chem.*, 1997, 36, 472.
- 22 H. Oku, N. Ueyama and A. Nakamura, Chem. Lett., 1996, 1131.
- 23 A. Cervilla, E. Llopis, A. Ribera, A. Doménech and E. Sinn, J. Chem. Soc., Dalton Trans., 1994, 3511.