Dalton Communications

Crystal Structure and Oxo-transfer Properties of $[NH_4]_2[W^{VI}O_2\{O_2CC(S)Ph_2\}_2]$

Antonio Cervilla,[*,a] **Elisa Llopis,**[a] **Antonio Ribera,**[a] **Antonio Doménech**[a] **and Ekkehard Sinn**[b]
[a] *Departament de Química Inorgànica, Universitat de València, Dr. Moliner 50, 46100 Burjassot (València), Spain*
[b] *School of Chemistry, University of Hull, Kingston upon Hull HU6 7RX, UK*

The complex $[NH_4]_2[W^{VI}O_2\{O_2CC(S)Ph_2\}_2]$ is the first example of a non-dithiolene tungsten complex capable of oxidising benzoin to benzil in methanol; the reduced complex product formed, presumably a monomeric $W^{IV}O$ species, was reoxidised with nitrate ions, regenerating the starting $W^{VI}O_2$ complex which then acts as a true homogeneous catalyst.

Although tungsten and molybdenum possess quite similar chemistries, only recently has a variety of tungsten-containing enzymes been found,[1] *e.g.*, formate dehydrogenase, carboxylic acid reductase (aldehyde oxidase) and aldehyde oxidoreductase (aldehyde ferredoxin oxidoreductase). However, contrary to molybdenum, the lack of well characterised $W^{VI}O_2$ and $W^{IV}O$ compounds has hampered the acquisition of information on tungsten-mediated oxo-transfer reactions.[2] Indeed, model compounds for the tungsten enzymes are extremely rare.[3] The structural characterisation and reactivity of tungsten-(VI), -(V) and -(IV) complexes containing benzenedithiolate ligands has focused on proposing models for oxo-tungsten active sites of enzymes.[4] In this regard it is worth noting that $[W^{IV}O(S_2C_6H_4)_2]^{2-}$ can be readily oxidised by trimethylamine *N*-oxide to give the stable *cis*-$[W^{VI}O_2(S_2C_6H_4)_2]^{2-}$ complex, which is, in turn, capable of reacting with benzoin to regenerate the starting $W^{IV}O$ complex.[4] This apparently indicates that 'dithiolene-like' benzenedithiolate ligands facilitate the reversible tungsten(VI)–tungsten(IV) conversion. In fact, the lack of tungsten model compounds has been correlated with the more negative reduction potential of the W^{VI}–W^{IV} couple, which is also why tungsten is best known as a molybdenum antagonist in enzymatic systems.[5]

Our previous studies on the chemistry of relevant oxo-molybdenum model compounds of hydroxylase enzymes have centred on the synthesis and reactivity of molybdenum-(VI),[6] -(V)[7] and -(IV)[8] complexes derived from 2,2-diphenyl-2-sulfanylacetic acid, thiobenzilic acid $[Ph_2C(SH)CO_2H]$. All three complexes have been structurally characterised. We now report the synthesis and structure of an homologous tungsten complex $[NH_4]_2[W^{VI}O_2\{O_2CC(S)Ph_2\}_2]$ **1**,† which constitutes the first example of a tungsten(VI) species possessing a $WO_2(O_2S_2)$ donor set. As deduced from tungsten EXAFS (extended X-ray absorption fine structure) analysis,[1f] this environment is compatible with the co-ordination unit found in some tungstoenzymes such as that present in the oxidised form of aldehyde ferredoxin oxidoreductase, $WO_2[S_{2,3}(O/N)]$. The capability of compound **1** to oxidise organic phosphines, thiols and benzoin has been also explored. The findings suggest that only benzoin is readily oxidised to benzil by **1**, yielding a monomeric $W^{IV}O$ complex. Nitrate ions can be used to regenerate the starting $W^{VI}O_2$ complex by reoxidising this $W^{IV}O$ complex product. Catalytic cycles for the oxidation of benzoin by nitrate ions are also developed.

X-Ray crystallography‡ shows that the complex anion of **1** adopts a distorted octahedral molecular structure containing a *cis*-WO_2 group co-ordinated to two equivalent, fully deprotonated ligand molecules (Fig. 1). The corresponding molybdenum complex has an essentially identical geometry.[6] The sulfur atoms are *trans* to each other and *cis* to the terminal oxo groups, with W=O, W–S and W–$O_{carboxy}$ bond lengths averaging 1.723(7), 2.419(4) and 2.140(7) Å, respectively. All these parameters are compatible with those found in the oxidised form of some tungsten oxidoreductase enzymes by EXAFS analysis (W=O 1.74, W–S 2.41 and W–O/N 2.16 Å).[1f]

Compared with its homologous molybdenum complex (λ_{max} = 370 nm), yellowish methanolic solutions of **1** exhibit a significant blue-shifted UV/VIS absorption maximum at 310 nm ($\varepsilon \approx 5.000$ dm^3 mol^{-1} cm^{-1}) that should be assigned as a ligand-to-metal charge-transfer band. A similar shift was previously observed in $[MO_2(S_2C_6H_4)_2]^{2-}$ (M = Mo or W).[4]

The oxo-transfer properties of **1** were investigated in

---

† The compound $Ph_2C(SH)CO_2H$ (1 g, 4 mmol) in methanol (25 cm^3) was slowly added to a stirred solution of $Na_2WO_4 \cdot 2H_2O$ (0.68 g, 2 mmol) dissolved in water (8 cm^3) containing NH_4Cl (0.22 g, 4 mmol). The resulting solution turned yellow, yielding crystals on cooling to 5 °C and allowing to stand for 24–48 h. The yellow product was purified by recrystallisation from ethanol–water (44% yield).

‡ *Crystal data.* $[NH_4]_2[WO_2\{CO_2C(S)Ph_2\}_2] \cdot 2H_2O$, $M = 772.54$, monoclinic, space group $P2_1/c$, $a = 8.151(6)$, $b = 14.386(9)$, $c = 24.869(20)$ Å, $\beta = 92.36(4)°$, $U = 2914(6)$ Å^3, $Z = 4$, $F(000) = 1536$, $D_c = 1.761$ g cm^{-3}, λ(Mo-Kα) = 0.710 69 Å, μ(Mo-Kα) = 42.36 cm^{-1}, crystal size 0.38 × 0.34 × 0.28 mm. The intensities of 7487 reflections were measured at room temperature ($0 \leqslant 2\theta \leqslant 55.2°$) on a Rigaku AFC6S diffractometer using monochromated Mo-Kα radiation. Corrections were applied for absorption using DIFABS[9] and for Lorentz-polarisation. The heavy-atom position, determined from a Patterson function, phased the data well enough to permit location of the other non-hydrogen atoms from successive Fourier-difference functions. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 4017 observed reflections [$I > 3.0\sigma(I)$] and 365 variable parameters and converged with unweighted and weighted [$w = 4F_o^2/\sigma^2(F_o^2)$] agreement factors of: $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.047$ and $R' = [\Sigma w(|F_o| - |F_c|^2)/\Sigma F_o^2]^{\frac{1}{2}} = 0.047$. All calculations were performed using the TEXSAN[10] software package. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre, see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

methanol by means of spectrophotometric, gas chromatographic and NMR techniques. No reaction was evidenced with typical oxo acceptors such as triphenylphosphine or thiophenol in the temperature range 25–60 °C. More basic phosphines such as PMe_2Ph turn the initially yellow solution of **1** blue, but ^{31}P and ^{13}C NMR spectra showed complex decomposition and formation of thiophosphine. This lack of reactivity contrasts with the behaviour of the analogous molybdenum complex, which reacts with all these substrates at room temperature to yield the ESR-active molybdenum(v) complex $[Mo^VO\{O_2CC(S)Ph_2\}_2]^-$, and the corresponding phosphine oxide or disulfide.[11] The stoichiometric ratio of consumed phosphine (PR_3) or thiol (RSH) to initial $Mo^{VI}O_2$ complex concentration is in agreement with equation (1).

$$2[Mo^{VI}O_2\{O_2CC(S)Ph_2\}_2]^{2-} + PR_3\,(2RSH) + 2H^+ \longrightarrow 2[Mo^VO\{O_2CC(S)Ph_2\}_2]^- + P(O)R_3\,(RSSR + H_2O) + H_2O \quad (1)$$

Benzoin was also examined as reductant of **1**, ^{13}C and ^1H NMR spectroscopy and gas chromatography demonstrating that benzoin was oxidised to benzil. In systems initially containing 2.5×10^{-3} mol dm^{-3} **1** and 5–15 equivalents of benzoin, the reaction proceeded in 24–48 h at 40 °C to afford a deep red ($\lambda_{max} = 531$ nm) ESR-silent complex solution containing > 90% of benzil based on the quantitative reduction of **1** [equation (2)]. Interestingly, the reaction rate is greatly reduced when dimethylformamide (dmf), instead of methanol, is used as the solvent under similar experimental conditions.

$$[W^{VI}O_2\{O_2CC(S)Ph_2\}_2]^{2-} + PhC(O)CH(OH)Ph \longrightarrow [W^{IV}O\{O_2CC(S)Ph_2\}_2]^{2-} + PhC(O)C(O)Ph + H_2O \quad (2)$$

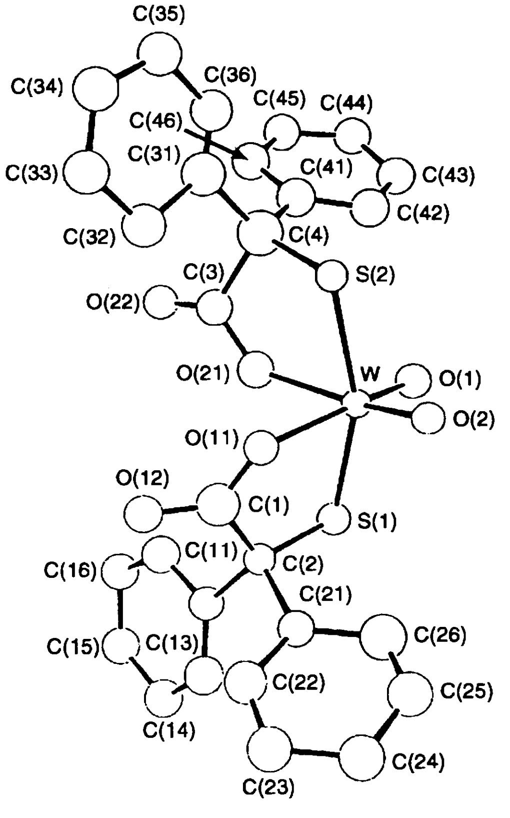


Fig. 1 Structure of $[WO_2\{O_2CC(S)Ph_2\}_2]^{2-}$ and the atom labelling scheme. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): W–S(1) 2.434(4), W–S(2) 2.405(4), W–O(1) 1.716(7), W–O(2) 1.731(7), W–O(11) 2.129(7), W–O(21) 2.152(7), S(1)–W–S(2) 159.7(1), S(1)–W–O(1) 89.0(3), S(1)–W–O(2) 87.6(3), S(1)–W–O(11) 77.6(3), S(1)–W–O(21) 86.0(3), O(1)–W–O(2) 103.1(3), O(1)–W–O(11) 163.1(3), O(1)–W–O(21) 91.8(3), O(11)–W–O(21) 77.4(3)

Reaction (2) was confirmed by combining equimolar quantities of **1** and benzoin, which produced the identical chromophore and the total oxidation of benzoin. Further, cyclic voltammetry, using a glassy carbon electrode and 0.1 mol dm^{-3} NBu_4PF_6 as supporting electrolyte, on the resulting complex solution showed a single irreversible oxidation centred at +0.45 V *vs.* SCE. This value is comparable to that found for the oxidation of $[W^{IV}O\{S_2C_2(CN)_2\}_2]$ in MeCN.[12]

Having established the oxo transfer from **1** to benzoin, the reverse process was examined using nitrate ions. It was found that NO_3^- reacted rapidly with the reduced tungsten-containing species to give the initial yellow solution of complex **1**. Nevertheless, no attempts were made to obtain spectrophotometric yields since benzoin, benzil, and **1** absorb in the same spectral region (300–400 nm).

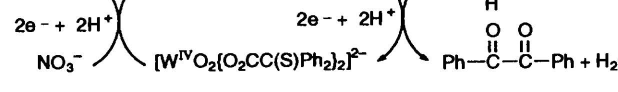
The observed nitrate reduction reaction is not unexpected because $W^{IV}O$ complexes have been postulated to act as avid oxo acceptors. In fact, the first well documented tungsten-mediated oxygen-atom transfer corresponded to the $W^{IV} \longrightarrow W^{VI}$ transformation involving $[W^{IV}(OC_6H_3Me_2\text{-}2,6)_4]$ and cyclohexene epoxide.[13] The above mentioned oxidation of $[W^{IV}O(S_2C_6H_4)_2]^{2-}$ by trimethylamine *N*-oxide constitutes another demonstration of the feasibility of such a transformation. Yet, it should be pointed out that the tungsten(IV)-mediated reduction of nitrate ions has not been realised in any system. The only biologically relevant nitrate to nitrite reduction is that performed by the sterically hindered complex $[Mo^{IV}O(L)(dmf)]$ [H_2L = 2,6-bis(2,2-diphenyl-2-sulfanylethyl)pyridine].[14]

The successful oxo-transfer reaction from $W^{VI}O_2$ to benzoin and from nitrate to $W^{IV}O$ suggests the coupling of both reactions to form the catalytic cycle shown in Scheme 1 with a net reaction (3).

$$NO_3^- + PhC(O)CH(OH)Ph \longrightarrow NO_2^- + PhC(O)C(O)Ph + H_2O \quad (3)$$

In a typical experiment, 3–10 × 10^{-2} mmol of **1** and 15–50 equivalents of benzoin were stirred in deaerated methanol (27 cm^3) containing an excess of ammonium nitrate at 40 °C. The kinetics of the system were analysed by gas chromatography which allowed the identification and quantitation of both benzoin and benzil. The total sum of their integrated intensities was constant during the entire course of the reaction.

Time–concentration curves demonstrate two important properties of the catalytic system. First, the benzoin oxidation rate is linearly dependent on the concentration of **1**, indicating that the catalysis is based on tungsten-mediated oxo-transfer chemistry rather than on some nonspecific process. Moreover, suitable controls demonstrated no detectable reaction in the absence of **1**. Secondly, if benzoin oxidation is the rate-limiting reaction under these conditions, the consumption of benzoin should be first order in both [benzoin] and [**1**]. Because the regeneration of complex **1** is relatively fast, its concentration should be essentially constant throughout the reaction. Thus, the disappearance of benzoin should follow the rate equation $[\text{benzoin}] = [\text{benzoin}]_0\, e^{-k[\mathbf{1}]\cdot t}$, where the subscript denotes initial concentration. This relationship can also be expressed in a logarithmic form, a plot of which is presented in Fig. 2. It can be seen that the rate of disappearance of benzoin could be



Scheme 1

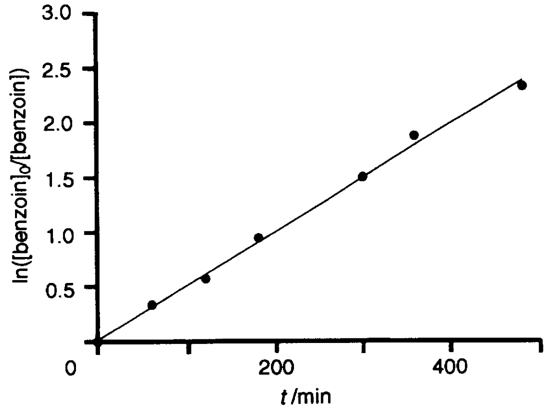


Fig. 2 Plot of ln([benzoin]$_0$/[benzoin]) *vs.* time for systems containining initially 4.5×10^{-2} mol dm^{-3} benzoin, 2.5×10^{-3} mol dm^{-3} $[NH_4]_2[WO_2\{O_2CC(S)Ph_2\}_2]$ and 0.14 mol dm^{-3} NH_4NO_3 in methanol (27 cm^{-3}); T = 40 °C

described by a first-order rate law ($K_{obs} = k[\mathbf{1}] = 4.9 \times 10^{-3}$ min^{-1}, T = 313 K, [**1**] = 2.5×10^{-3} mol dm^{-3}).

These results demonstrate that thiocarboxylate co-ordination to $W^{VI}O_2$ or $W^{IV}O$ gives complexes whose properties are similar to those of dithiolene-containing complexes which are considered to be good models for tungstooxidase enzymes. In addition, the present study is the first report of a tungsten-based catalyst for the reduction of nitrate ions. Appropriate kinetic experiments are in progress in order to evaluate the rate constants for the catalytic cycle proposed in Scheme 1.

Acknowledgements

This research was supported by the Dirección General de Investigación Científica y Técnica (grant PB92-0872). We also thank the European Communities, Directorate General XII (MASIMO program), for financial assistance. A. R. thanks Generalitat Valenciana for a postgraduate scholarship.

References

1 (*a*) I. Yamamoto, T. Sasaki and L. G. Ljundahl, *J. Biol. Chem.*, 1983, **253**, 1826; (*b*) H. White, G. Strobl, R. Feicht and H. Simon, *Eur. J. Biochem.*, 1989, **184**, 89; (*c*) S. Munkund and M. W. W. Adams, *J. Biol. Chem.*, 1990, **265**, 11508; (*d*) S. Munkund and M. W. W. Adams, *J. Biol. Chem.*, 1991, **266**, 14208; (*e*) G. N. George, Y. Gea, R. C. Prince, S. Munkund and M. W. W. Adams, *J. Inorg. Biochem.*, 1991, **43**, 241; (*f*) G. N. George, R. C. Prince, S. Munkund and M. W. W. Adams, *J. Am. Chem. Soc.*, 1992, **114**, 3521.
2 S. Yu and R. H. Holm, *Inorg. Chem.*, 1989, **28**, 4385; K. R. Dunbar and G. M. Finniss, *Coord. Chem. Rev.*, 1993, **127**, 65.
3 J. H. Enemark and C. G. Young, *Adv. Inorg. Chem.*, 1994, **40**, 1.
4 N. Ueyama, H. Oku and A. Nakamura, *J. Am. Chem. Soc.*, 1992, **114**, 7310.
5 J. L. Johnson, K. V. Rajagopalan and H. J. Cohen, *J. Biol. Chem.*, 1974, **249**, 859; J. L. Johnson, H. J. Cohen and K. V. Rajagopalan, *J. Biol. Chem.*, 1974, **249**, 5046.
6 P. Palanca, T. Picher, V. Sanz, P. Gómez-Romero, E. Llopis, A. Doménech and A. Cervilla, *J. Chem. Soc., Chem. Commun.*, 1990, 531.
7 V. Sanz, T. Picher, P. Palanca, E. Llopis, J. A. Ramírez, D. Beltrán and A. Cervilla, *Inorg. Chem.*, 1991, **30**, 3115.
8 A. Cervilla, E. Llopis, J. A. Ramírez, A. Doménech, P. Palanca, M. T. Picher, C. A. Ghilardi and A. Orlandini, *J. Chem. Soc., Dalton Trans.*, 1994, 175.
9 DIFABS, N. G. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
10 TEXSAN, Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985.
11 E. Llopis, A. Doménech, J. A. Ramírez, A. Cervilla, P. Palanca, T. Picher and V. Sanz, *Inorg. Chim. Acta*, 1991, **189**, 29.
12 S. Sarkar and S. K. Das, *Proc. Indian Acad. Sci.*, 1992, **104**, 175.
13 M. L. Listemann, R. R. Schrock, J. C. Dewan and R. M. Kolodziej, *Inorg. Chem.*, 1988, **27**, 264.
14 J. A. Craig and R. H. Holm, *J. Am. Chem. Soc.*, 1989, **111**, 2111.

Received 30*th September* 1994; *Communication* 4/05818F