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Aminobisphenolate supported tungsten disulphido and dithiolene complexes

Cite this: DOI: 10.1039/xoxxoooooox

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Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

www.rsc.org/

Dioxotungsten(VI) complexes with tetradentate amino bisphenolates were converted into the corresponding C_s-symmetric amino bisphenolate disulphido complexes by a reaction with either Lawesson's reagent or P_2S_5. Further reaction with diethyl acetylenedicarboxylate leads to the formation of diamagnetic tungsten(IV) dithiolene compounds. The syntheses, crystal structures, spectroscopic and electrochemical characterization of such disulphido and dithiolene complexes are presented.

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Introduction

Tungsten is the only third row transition metal that has a clear role in biology showing biochemical functions related to that of molybdenum.[1] Both tungsten and molybdenum are found in enzymes which catalyse oxo-transfer redox reactions, where the covalent bonds between oxygen and carbon atoms are broken or formed. In such biological processes, the destination or the source of the oxygen atom is typically water.[2] While molybdenum is required as a trace element by essentially all forms of life, tungsten is used only by some anaerobic micro-organisms, many of which are thermophilic.[1] In tungsten enzymes, the metal centre is coordinated to two organic molybdopterin cofactors.[2a] The metal-binding, chelating group of molybdopterin is dithiolene, *i.e.* an unsaturated and potentially non-innocent bidentate dianionic ligand where two donor atoms are both sulphur.[2b] Consequently, a moiety including the metal centre and one or two dithiolene ligands is one of the most common motifs in the molecular models for tungsten enzymes.[3,4] Although there are several ways to prepare metal complexes with dithiolene ligands, there are no routine procedures for tungsten dithiolenes.[5] A straightforward method is to employ the transmetallation reaction of the alkali metal salts of 1,2-alkenedithiolate with the metal halides.[5] Alternatively, if there are appropriate metal disulphido complexes available, the metal dithiolenes can be produced readily by the reaction of isolated metal disulphides with activated alkynes such as dimethyl acetylenedicarboxylate.[5-8] In the latter reactions, the formation of the five-membered ring structure is associated with a formally two-electron reduction of the metal centre. The number of tungsten(VI) disulphido complexes which are useful for the dithiolene synthesis is rather limited, obviously due to the lack of suitable disulphide precursors. The few examples on the molecular disulphidotungsten(VI) complexes are prepared using the oxo/sulphido substitution reaction of the corresponding dioxo complexes.[9-11] As there is no general procedure for the transformation of multiply bound terminal metal-oxo ligands to metal-sulphido ligands, a number of different sulphur compounds have been used. In regard to molybdenum and tungsten complexes, such reactions generally involve H_2S/HS^-,[12-16] B_2S_3,[9,10,17] P_2S_5,[10] $(R_3Si)_2S/R_3SiSH$[18-21] or Lawesson's reagent (2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulphide).[22,23]

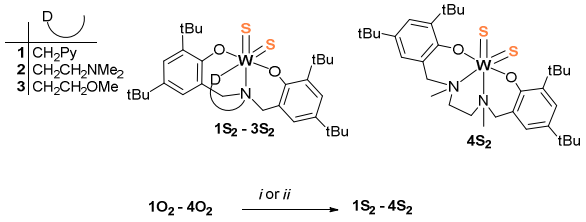
To learn more about tungsten sulphur chemistry and find potential model compounds for the active centres of tungsten enzymes, we prepared new tungsten complexes with terminal sulphide ligands as well as dithiolene derivatives. Here we describe the syntheses and characterisation of new aminobisphenolate supported tungsten disulphides by oxo/sulphido substitution reaction. The preparation of the corresponding dithiolene compounds by the reaction with activated alkyne is also reported as well as the electrochemical behaviour of generated tungsten(IV) dithiolenes.

Results and discussions

Synthesis

Oxide-for-sulphide substitution of Dioxotungsten

Dioxotungsten complexes[24] **$1O_2$** – **$4O_2$** were treated with potential sulphide sources, *i.e.* P_2S_5 and Lawesson's reagent to prepare aminobisphenolate supported disulphido complexes of tungsten(VI) (Scheme 1). The colourless solutions of dioxotungsten complexes in 1,2-dichloroethane were allowed to react with thionation reagents to undergo an oxo/sulphido substitution as indicated by a rapid colour change of the solutions to red. After the reactions were completed the products were isolated by column chromatography to obtain air-stable compounds as red or orange-red crystalline solids in moderate to high yields (73, 21, 35 and 71 % for **$1S_2$**, **$2S_2$**, **$3S_2$** and **$4S_2$**, respectively). Lawesson's reagent and P_2S_5 were both reactive under applied conditions although the use of Lawesson´s reagent required an elevated temperature whereas P_2S_5 reacted at room temperature. The reactions were repeated by using different stoichiometries, but no W(O)S complexes were found while the disulphido complexes were obtained as only isolable products. These air- and moisture-stable complexes are soluble in common organic solvents but insoluble in water. As expected on the basis of the substitution reaction, the IR spectra of **$1S_2$ - $4S_2$** lack the typical absorptions (at ca. 880-930 cm^{-1}) for *cis*-WO_2 precursors, but they show strong absorptions at 478 - 490 cm^{-1} supposedly due to the ν(W=S) stretches. The electronic spectra of these red disulphido complexes in acetonitrile show intense ultraviolet bands (λ_{max} 280 nm) with tailing (at *ca.* 500 nm) into the visible region. While the parent dioxides are colourless, the intense colours of these formally d^0 tungsten(VI) disulphide complexes arise from the ligand-to-metal charge-transfer transitions related to the terminal sulphido ligands.



Scheme 1 Syntheses of disulphido complexes. (*i*) 1,2-$C_2H_4Cl_2$, Lawesson's reagent, 60-80 °C, 20 h (for **$1S_2$ – $3S_2$**) (*ii*) 1,2-$C_2H_4Cl_2$, P_2S_5, 20 °C, 20 h (for **$3S_2$** and **$4S_2$**).

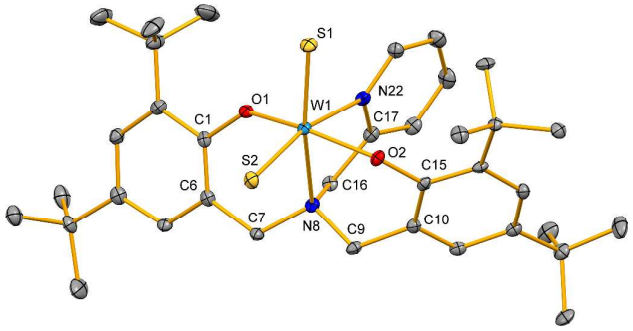


Fig. 1 The molecular structure of **1S$_2$**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are presented at the 30 % probability level (applies to all presented X-ray structures).

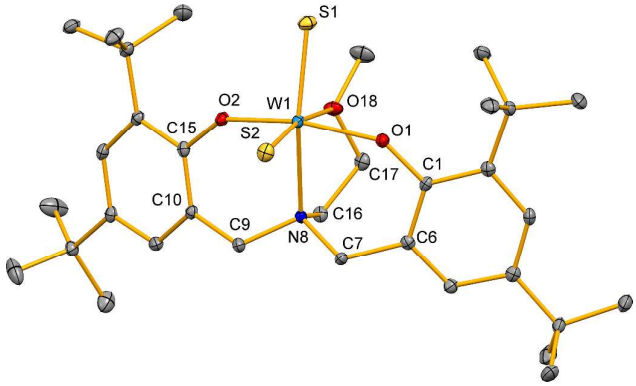


Fig. 2 The molecular structure of **3S$_2$**. Hydrogen atoms are omitted for clarity.

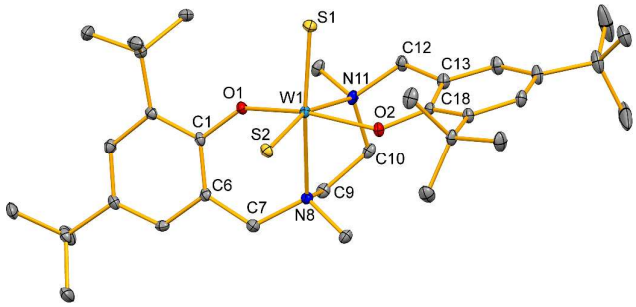


Fig. 3 The molecular structure of **4S$_2$**. Hydrogen atoms are omitted for clarity.

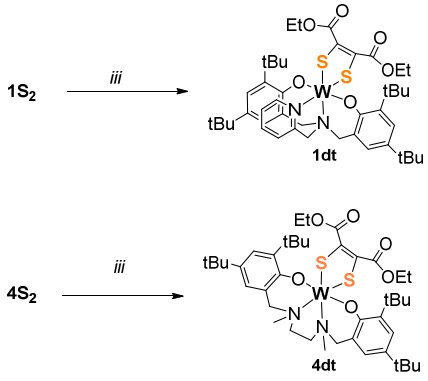
Table 1. Selected bond lengths (Å) and angles (°) for **1S$_2$**, **3S$_2$** and **4S$_2$**.

	1S$_2$	**3S$_2$**	**4S$_2$**
W1-S1	2.1698(11)	2.1646(7)	2.1593(8)
W1-S2	2.1695(10)	2.1657(8)	2.1689(7)
W1-O1	1.923(3)	1.9190(18)	1.9184(19)
W1-O2	1.934(3)	1.9017(18)	1.923(2)
W1-N8	2.378(3)	2.375(2)	2.409(2)
W1-N22/O18/N11	2.366(3)	2.471(2)	2.415(2)
S1-W1-S2	105.45(4)	105.24(3)	107.09(3)
O1-W1-O2	154.31(12)	155.63(8)	156.22(8)
S1-W1-N8	162.66(8)	156.49(6)	164.11(6)
S2-W1-N22/O18/N11	163.16(9)	167.70(5)	161.96(6)
N8-W1-N22/O18/N11	71.61(12)	69.44(7)	73.88(8)

The solid state structures of **1S$_2$**, **3S$_2$** and **4S$_2$** were verified by X-ray crystallography and the determined molecular structures are shown in Figs. 1-3, respectively. In the studied complexes, the overall geometry around the metal centre is closely similar to those reported for analogous Mo and W dioxo complexes with aminobisphenolates.[24-29] The nitrogen donor N8 is located *trans* to the terminal sulphido S1 with the relatively long W1-N8 bond (2.38 -2.41 Å) most likely due to the structural *trans* effect of a multiple bonded sulphido ligand. In all these compounds, the W=S bond lengths (2.16 – 2.17 Å), are typical for molecular tungsten sulphido complexes used as structural analogues of the oxidized sites in the xanthine oxidoreductase enzyme family.[10,16,21,30-32]

COMPLEXES 1S$_2$ AND 4S$_2$ TREATED WITH DIETHYL ACETYLENEDICARBOXYLATE

When dichloromethane solutions of disulphido complexes **1S$_2$** and **4S$_2$** were treated with a slight excess of diethyl acetylenedicarboxylate an immediate colour change from orange to green (**1S$_2$**) or dark red (**4S$_2$**) was observed. The reactions were complete after 15 minutes and pure products (according to the NMR spectra) were obtained in virtually quantitative yields by evaporating the volatiles in vacuum. The compounds are stable under ambient atmosphere and they can be dissolved in common organic solvents. High-quality crystals for X-ray analyses of **1dt** and **4dt** were formed from saturated acetonitrile solutions upon cooling (see Figs. 3 and 4). The W-O_{Ar} and W-N bond lengths are slightly shorter than in the disulphide precursors, otherwise the coordination of the bisphenolate ligands is closely similar. The overall geometry around the metal centre is related to that found in W(IV) dithiolene complex $[W(OSiPh_3)_2(Me_4phen)(S_2C_2Ph_2)]$.[30] The compounds **1dt** and **4dt** are formally octahedral W(IV) complexes, so the metal centres may have either paramagnetic triplet or diamagnetic singlet d^2 electron configurations. For strongly tetragonally compressed octahedral d^2 complexes the orbital splitting is known to result the singlet ground state system with both electrons on the d_{xy} orbital.[33] In this study, the two W(IV) complexes structures have axially compressed octahedral structures with four long bonds in xy-planes planes (S1, S2, N8, N11 in **1dt** and S1, S2, N8, N22 in **4dt**) and two shorter ones (O1, O2) along z axes. This leads to a diamagnetic, singlet ground state with two electrons on d_{xy} orbital. The diamagnetic ground state of the W(IV) complexes allows the measurements of the NMR spectra of **1dt** and **4dt** with a good resolution.[34] The electronic spectrum of greenish-yellow **1dt** in $CHCl_3$ show intense ultraviolet bands (λ_{max} 270, 330 and 380 nm) and a weak visible absorption at 470 nm. Similarly, brownish-red **4dt** has two strong UV absorptions (λ_{max} 310 and 375 nm) and a weak absorption in the visible region (λ_{max} 510).



Scheme 2 Syntheses of dithiolene complexes. (*iii*) CH_2Cl_2, diethyl acetylenedicarboxylate, 20 °C, 30 min.

NMR spectroscopy

The structures of dithiolene complexes **1dt** and **4dt** were investigated in $CDCl_3$ solution with ^1H and ^{13}C NMR spectroscopy and they were found to resemble the solid state structures. The ^1H and ^{13}C chemical shift assignment was achieved with the help of 2D homo- and heteronuclear correlation techniques (COSY, NOESY, HSQC, HMBC). The assignment, given in the Experimental section, corresponds to the atom numbering shown in Figs. 4 and 5. 1D NOESY experiments with multiple mixing times (0.25–1.00 s) were conducted in order to assign the ^1H signals of the diastereotopic geminal CH_2 hydrogens with correct stereochemistry: For **1dt**, the suffix "syn" refers to the CH_2 hydrogen pointing towards the *N*-pyridinylmethyl group, whilst "anti" points away from it. For **4dt**, "syn" CH_2 hydrogens are on the same side of their ring with the nearest *N*-methyl group; the diastereotopic OCH_2CH_3 methylene proton shifts (4.34 and 4.33 ppm) could not be stereoassigned and are labelled with "A" and "B", respectively. The NMR spectra of **1dt** are consistent, regarding the number and intensities of signals, with its expected structure assuming C_s symmetry, with an effective plane of symmetry defined by the central metal and its sulphur and nitrogen ligand atoms. The heavy atoms of the pyridinyl methyl group and the sulphur-containing ligand reside in this plane while the two phenolate arms are out of the plane and chemically equivalent. Thus, for example the C16-H_2 hydrogens are enantiotopic and chemically equivalent, producing a two-hydrogen singlet at 4.44 ppm. Likewise, the CH_2 hydrogens in each OCH_2CH_3 group are enantiotopic and appear as simple two-hydrogen quartets at 4.43 and 4.38 ppm.

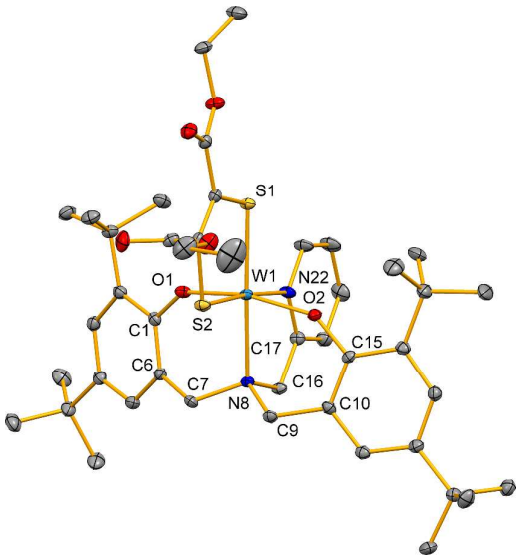


Figure 4. The molecular structure of **1dt**. Hydrogen atoms are omitted for clarity.

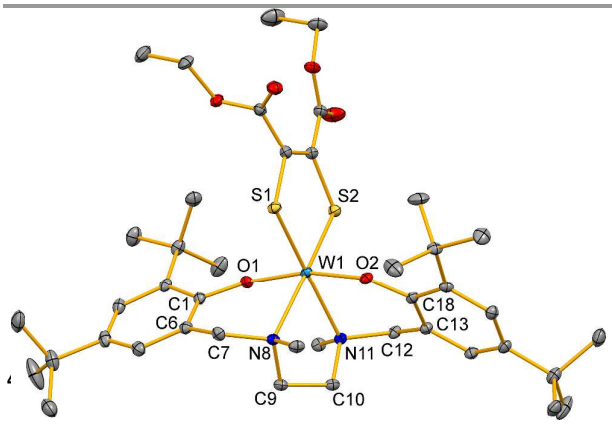


Figure 5. The molecular structure of **4dt**. Only one of the two crystallographically independent molecules is shown. Hydrogen atoms are omitted for clarity.

The two $C(S)C(O)OCH_2CH_3$ parts of the sulphur-containing ligand, however, are not chemically equivalent and thus have slightly different ^1H and ^{13}C chemical shifts. The C7-H_2 hydrogens are diastereotopic and yield two doublets at 4.37 (syn) and 4.83 (anti) ppm; these are chemically equivalent to the syn and anti hydrogens of C9-H_2, respectively. An NOE correlation between 21-H and 2-*t*Bu/14-*t*Bu indicates that these parts remain spatially close in $CDCl_3$ solution, i.e. the neutral pyridinyl ligand remains coordinated to the metal.

Table 2. Selected bond lengths (Å) and angles (°) for **1dt** and **4dt.**

	1dt	**4dt**[a]
W1-S1	2.3112(10)	2.3197(5)
W1-S2	2.3390(10)	2.3210(5)
W1-O1	1.893(3)	1.8916(15)
W1-O2	1.891(3)	1.921(15)
W1-N8	2.303(3)	2.3312(18)
W1-N22/N11	2.222(4)	2.3026(18)
C44-C45/ C42-C43	1.343(6)	1.339(3)
S1-W1-S2	85.12(4)	85.471(19)
O1-W1-O2	162.68(12)	166.65(7)
S1-W1-N8	174.86(9)	172.06(5)
S1-C44-C45-S2/ S1-C42-C43-S2	-4.8(5)	0.9(3)

[a] One of the two crystallographically independent molecules.

The NMR spectra of **4dt** similarly reveal the presence of an effective symmetry; for this molecule it is a C_2 axis going through the central W atom and bisecting the C9–C10 and C(S)=C(S) bonds. All the geminal CH_2 hydrogens in this chiral molecule are thus diastereotopic and show different chemical shifts (including those in the OCH_2CH_3 groups). The two halves of the S-containing ligand are now chemically equivalent *via* this symmetry, as are the two halves of the bisphenolate ligand. The resulting chemical shift equivalence leaves an ambiguity in the interpretation of the observed NOE correlations. However, all the NOEs can be interpreted in a way that is consistent with the crystal structure of **4dt**. For example, an NOE between the ^1H signals at 1.09 and 2.92 ppm was observed; obviously, this is due to C2-*t*Bu and N11-CH_3 being spatially close to each other in the molecular structure (rather than C2-*t*Bu and N8-CH_3). In the same fashion, the observed NOEs indicate that N8-CH_3 and C10-H_{anti} are close; as are C7-H_{anti} and C9-H_{syn}. The ^1H and ^{13}C NMR spectra of $\mathbf{1S_2 - 4S_2}$ are consistent with the supposed distorted octahedral structures and they present typical resonances for C_s-symmetric aminobisphenolate complexes similarly to the fully characterised parent dioxo complexes.[24]

Electrochemistry

The electrochemical behaviour of complexes **1dt** and **4dt** was investigated using the cyclic voltammetric technique (CV). The CV data obtained in this work are listed in Table 3. Fig. 6a shows the CVs for **1dt** and **4dt** when using 50 mV/s as a scan rate. As can be seen from the CVs the complexes exhibit a rather similar redox-chemistry. On the positive scan two well-defined oxidation peaks, I and II, are formed. When reversing the scan one reduction peak, I', can be observed for **1dt** whereas **4dt** also shows a small reduction peak marked with II'.

In Fig. 6b the anodic scan for **1dt** is limited to the first oxidation peak showing a quasi-reversible redox couple I /I' with $E_{1/2}$= 0.37 V. As observed from Fig. 6b this first oxidation process is diffusion controlled as the peak heights are correlated to the scan rates. This is observed for both complexes and the redox couple I /I' can be ascribed to a one-electron oxidation of W^{IV} to W^{V}. It has, however, to be mentioned that based on the CV measurements alone it is not possible to rule out that the observed changes in the voltammogram could be due to the oxidation of the ligand rather than the metal. No colour change could be observed during the electrochemical measurements.

The second oxidation step (II) in the potential range of 1.3 V for **1dt** and at 1.15 V for **4dt** (Fig. 6a) is totally irreversible at all sweep rates studied (0.05-0.2 Vs^{-1}) showing no shift in peak potential upon increasing the scan rate. The irreversibility of the curves suggests the instability of the generated species under electrochemical time scale. Cycling the potential to the negative range (from 0 to -1.5 V) gives no significant current changes in the CV indicating that no redox reactions take place in this particular potential range. When the potential is cycled in the positive range after such a negative potential scan, no changes can be observed for the peak potentials or peak separations for the redox couple I /II' or for II'. Neither new oxidation peaks can be observed in the CVs.

Table 3. The electrochemical potentials for complexes **1dt** and **4dt**.

Compound	E_{pa}(I)	E_{pa}(II)	E_{pc}(I')	E_{pc}(II')
1dt	0,43	1,31	0,35	
4dt	0,42	1,15	0,33	1,04

10^{-3} M solutions of compounds in 0.1 M of $TBAClO_4$ in MeCN. Scan rate: 100 mV/s, E values given in (V vs. Ag/AgCl). E_{pa} and E_{pc} indicates the anodic and cathodic peak potentials, respectively.

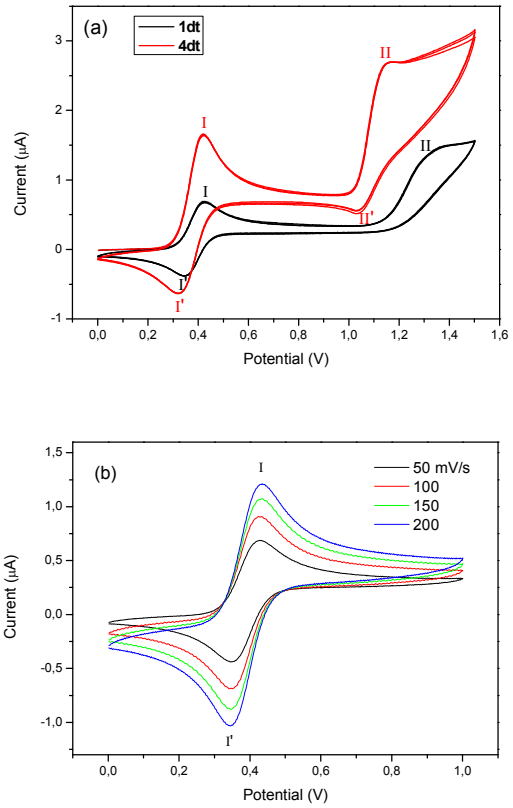


Fig. 6 (a) Cyclic voltammograms of complexes **1dt** and **4dt** in MeCN and 0.1 M $TBAClO_4$ as supporting electrolyte using 50 mV/s as scan rate. (b) Cyclic voltammograms of complex **1dt** in MeCN at increasing scan rates of 50, 100, 150 and 200 mV/s.

Conclusions

Disulphidotungsten(VI) complexes with tetradentate amino bisphenolates were prepared as molecular models of isolated disulphide centres of tungsten enzymes. The reaction of dioxotungsten(VI) complexes with thionation reagents (Lawesson's reagent and P_2S_5) lead to the oxo/sulphido substitution and formation air- and moisture-stable disulphido complexes. Isolated disulphidotungsten(VI) compounds have similar C_s-symmetric solution and solid-state structures as their dioxo precursors whereas the properties of W=S bonds match with tungsten sulphido complexes used as structural analogues for the oxidized sites in the xanthine oxidoreductase enzyme family. Further reactions of disulphidotungsten(VI) compounds with diethyl acetylenedicarboxylate yield dithiolene chelates in high yields. The reaction of disulphido species with activated alkyne is associated with the formal reductions of the metal centres leading to the formation of diamagnetic tungsten(IV) dithiolenes with a compressed octahedral structure in solid state. The bonding modes of these dithiolene ligands resemble those found for the chelating group of molybdopterin cofactor.

Experimental

Dioxotungsten complexes **$1O_2$** – **$4O_2$** were prepared from tetradentate aminobisphenol ligands and tris(1,2-ethanediolato)tungsten(VI) following a known procedure.[24]

Other chemicals and solvents were of commercial origins and were used without further purification. Samples for infrared spectroscopy were measured on a Bruker PMA50 FT-IR Spectrometer using an ATR setup. The UV spectra were measured in $CHCl_3$ solutions using Agilent Technologies Cary 60 UV-Vis spectrometer.

Syntheses of disulphido complexes $1S_2$ – $4S_2$.

The dioxotungsten complexes and sulphide precursors were dissolved in 1,2-dichloroethane and the reaction mixtures were stirred for 20 hours. Oxo-for-sulphide substitutions were carried using either Lawesson's reagent at 60-80 °C (Method 1) or P_2S_5 at room temperature (Method 2). The red or orange-red products were isolated by silica column chromatography using CH_2Cl_2 (**$1S_2$ – $3S_2$**) or toluene (**$4S_2$**) as an eluent. Compounds can be further purified by re-crystallisation from hot acetonitrile. Crystals of **$3S_2$** for X-ray studies were obtained from CH_2Cl_2 solution upon slow evaporation.

$1S_2$: Method 1 using 520 mg (0.69 mmol) of **$1O_2$** and 393 mg (0.97 mmol) of Lawesson´s reagent gave 397 mg (73 %) of red solid. IR: 2956s, 1606s (br), 1477s, 1443s, 1414w, 1390w, 1362m, 1304m, 1257s, 1240s, 1205m, 1171m, 1130m, 1095w, 1057w, 1018m, 975w, 914m, 852s, 808m, 760s, 729w, 696w, 645w, 634w, 588w, 557s, 478s ν(W=S) cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.37 (1H, d, *J* = 5.5 Hz, ArH), 7.47 (1H, dt, *J* = 1.4 Hz, *J'* = 7.6 Hz, ArH), 7.27 (1H, t, *J* = 7.6 Hz, ArH), 7.19 (2H, d, *J* = 2.3 Hz, ArH), 7.06 (1H, t, *J* = 6.2 Hz, ArH), 6.89 (2H, d, *J* = 2.3 Hz, ArH), 6.70 (1H, d, *J* = 7.8 Hz, ArH), 5.29 (2H, d, *J* = 13.2 Hz, CH_2), 4.08 (2H, CH_2), 3.67 (2H, d, *J* = 13.3 Hz, CH_2), 1.34 (18H, tBuH), 1.26 (18H, tBuH). ^{13}C NMR ($CDCl_3$): d 159.09, 157.23, 155.18, 142.97, 138.86, 138.54, 123.99, 123.92, 122.79, 121.18, 120.50, 65.69, 61.83, 35.00, 34.26, 31.61, 29.99. UV/vis, λ_{max} (ε, $dm^3mol^{-1}cm^{-1}$) 275 (23300), 370 (14000) nm. Anal. Calcd. (%) for $C_{36}H_{50}N_2O_2S_2W$ (790.77 g/mol): C, 54.68; H, 6.37; N, 3.54. Found: C, 54.15; H, 6.57; N, 3.09

$2S_2$: Method 1 using 596 mg (0.81 mmol) of **$2O_2$** and 326 mg (0.81 mmol) of Lawesson´s reagent yielded 130 mg (21 %) of red solid. IR: 2958s, 2868s, 1635s (br), 1473s, 1444s, 1412w, 1392w, 1362m, 1294w, 1257s, 1238s, 1205m, 1169m, 1130w, 1099w, 1047w (br), 912m, 872m, 854s, 835m, 806m, 779w, 754m, 555m, 485s ν(W=S) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.39 (2H, d, *J* = 2.5 Hz, ArH), 6.94 (2H, d, *J* = 2.4 Hz, ArH), 4.46 (2H, d, *J* = 14.2 Hz, CH_2), 3.91 (2H, d, *J* = 14.2 Hz, CH_2), 2.93 (2H, t, *J* = 5.3 Hz, CH_2), 2,79 (6H, NCH_3), 2.73 (2H, t, *J* = 5.0 Hz, CH_2), 1.54 (18H, tBuH), 1.31 (18H, tBuH). ^{13}C NMR ($CDCl_3$): δ 162.02, 143.34, 137.08, 123.96, 123.08, 123.00, 64.92, 58.89, 56.01, 51.48, 35.14, 34.30, 31.66, 30.87. UV/vis, λ_{max} (ε, $dm^3mol^{-1}cm^{-1}$) 280 (14000), 360 nm (7290). Anal. Calcd. (%) for $C_{34}H_{54}N_2O_2S_2W$ (770.78 g/mol): C, 52.98; H, 7.06; N, 3.63. Found: C, 52.64; H, 7.07; N, 3.59

$3S_2$: Method 1 using 483 mg (0.66 mmol) of **$3O_2$** and 265 mg (0.66 mmol) of Lawesson´s reagent yielded 177 mg (35 %) of red solid. Method 2 using 371 mg (0.52 mmol) of **$3O_2$** and 115 mg (0.51 mmol) of P_2S_5 gave identical product in a 149 mg (39 %) yield. IR: 2958s, 1635s (br), 1475s, 1414w, 1392w, 1362w, 1259s, 1240s, 1205m, 1173m, 1130w, 1103w, 1070w, 1032w, 916w, 860m, 808w, 760w, 561m, 490m ν(W=S), 469w cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.42 (2H, d, J = 2.3 Hz, ArH), 6.91 (2H, d, J = 2.2 Hz, ArH), 5.12 (2H, d, J = 13.7 Hz, CH_2), 3.68 (3H, OCH_3), 3.62 (2H, d, J = 13,7 Hz, CH_2), 3.20 (2H, t, J = 5.5 Hz, CH_2), 2.89 (2H, t, J = 5.5 Hz, CH_2), 1.50 (18H, tBuH), 1.32 (18H, tBuH). ^{13}C NMR ($CDCl_3$): δ 168.61, 143.55, 138.80, 124.59, 123.97, 121.50, 71.47, 67.10, 64.13, 54.67, 35.11, 34.43, 31.60, 29.78. UV/vis, λ_{max} (ε, $dm^3mol^{-1}cm^{-1}$) 300 (12000), 345 nm (9580). Anal. Calcd. (%) for $C_{33}H_{51}NO_3S_2W$ (757.74 g/mol): C, 52.31; H, 6.78; N, 1.85. Found: C, 52.54; H, 7.00; N, 1.69

$4S_2$: Method 2 using 595 mg (0.80 mmol) of $4O_2$ and 180 mg (0.80 mmol) of P_2S_5 yielded 439 mg (71 %) of orange-red solid. IR: 2958s, 1630s (br), 1471s, 1444s, 1362w, 1300w, 1238s, 1205m, 1171m, 1132m, 1065w, 914w, 850s, 812w, 758m, 615w, 584w, 555s, 482s ν(W=S), 459w cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.38 (2H, d, *J* = 2.2 Hz, ArH), 6.85 (2H, d, *J* = 2.2 Hz, ArH), 5.13 (2H, d, *J* = 14.5 Hz, CH2), 3.59 (2H, d, *J* = 14.7 Hz, CH_2), 3.32 (2H, d, *J* = 9.5 Hz, CH_2), 2.68 (6H, NCH_3), 2.30 (2H, d, *J* = 9.8 Hz, CH_2), 1.50 (18H, tBuH), 1.31 (18H, tBuH). ^{13}C NMR ($CDCl_3$): δ 157.77, 143.18, 138.86, 123.84, 123.75, 120.79, 67.86, 54.97, 49.51, 35.30, 34.32, 31.61, 30.57. UV/vis, λ_{max} (ε, $dm^3mol^{-1}cm^{-1}$) 285 (22000), 325 nm (11200). Anal. Calcd. (%) for $C_{34}H_{54}N_2O_2S_2W$ (770.78 g/mol): C, 52.98; H, 7.06; N, 3.63. Found: C, 52.60; H, 7.00; N, 3.39

Syntheses of dithiolene complexes 1dt and 4dt.

1dt: 100 mg of **$1S_2$** (0.13 mmol) was dissolved in 5 ml of CH_2Cl_2 and 50 µl of diethyl acetylenedicarboxylate (0.4 mmol) was added. The green solution was stirred for 30 min and then evaporated to obtain a pure product (according to the NMR spectra) in a nearly quantitative yield. The solid product was crystallised from 4 ml of hot acetonitrile to obtain 100 mg (89%) of **1dt** as greenish-yellow needles. IR: 2951m, 1719s, 1710s, 1680m, 1605w, 1548w, 1477s, 1447m, 1415w, 1390w, 1365m, 1297w, 1219vs (br), 1169s, 1128m, 1094w, 1061w, 1038s, 1020s, 974w, 939w, 914m, 874m, 860s, 811w, 774m, 762m, 746m, 691w, 669w, 652w, 593w, 568m, 527w, 511w, 475m cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 9.32 (1 H, br d, *J* = 5.3 Hz, 21-H), 7.59 (1 H, td, *J* = 1.4, 7.8, 7.8 Hz, 19-H), 7.18 (1 H, br m, 20-H), 7.05 (2 H, d, *J* = 2.2 Hz, 3-H & 13-H), 7.01 (1 H, br d, *J* =7.8 Hz, 18-H), 6.99 (2 H, d, *J* = 2.2 Hz, 5-H & 11-H), 4.82 (2 H, d, *J* = −12.9 Hz, 7-H_{anti} & 9-H_{anti}), 4.44 (2 H, s, 16-H_2), 4.43 (2 H, q, *J* = 7.2 Hz, OCH_2CH_3), 4.38 (2 H, q, *J* = 7.2 Hz, OCH_2CH_3), 4.38 (2 H, d, *J* = −12.8 Hz, 7-H_{syn} & 9-H_{syn}), 1.40 (3 H, t, *J* = 7.2 Hz, OCH_2CH_3), 1.37 (3 H, t, *J* = 7.2 Hz, OCH_2CH_3), 1.23 (18 H, s, 4-*t*Bu & 12-*t*Bu), 0.91 (18 H, s, 2-*t*Bu & 14-*t*Bu). ^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ 170.3, 168.62, 168.59, 167.3 (C(O)-C(S)=C(S)-C(O)), 164.1 (C17), 160.3 (C21), 156.8 (2 C, C1 & C15), 143.2 (2 C, C4 & C12), 140.4 (C19), 136.8 (2 C, C2 & C14), 124.7 (C20), 124.6 (2 C, C3 & C13), 124.4 (2 C, C5 & C11), 120.0 (C18), 119.8 (2 C, C6 & C10), 69.3 (2 C, C7 & C9), 63.3 (C16), 61.4 (OCH_2CH_3), 61.3 (OCH_2CH_3), 34.6 (2 C, 2-$C(CH_3)_3$ & 14-$C(CH_3)_3$), 34.4 (2 C, 4-$C(CH_3)_3$ & 12-$C(CH_3)_3$), 31.5 (6 C, 4-C(CH_3)$_3$ & 12-C(CH_3)$_3$), 29.4 (6 C, 2-C(CH_3)$_3$ & 14-C(CH_3)$_3$), 14.34 (OCH_2CH_3), 14.32 (OCH_2CH_3). UV/vis, λ_{max} (ε, $dm^3mol^{-1}cm^{-1}$) 270 (7450), 330 (5000), 380 nm (3200), 470 (500). Anal. Calcd. (%) for $C_{42}H_{64}N_2O_6S_2W$ (940.94 g/mol): C, 53.61; H, 6.86; N, 2.98. Found: C, 53.24; H, 6.67; N, 2.59.

4dt: 173 mg of **$4S_2$** (0.22 mmol) was dissolved in 5 ml of CH_2Cl_2 and 50 µl of diethyl acetylenedicarboxylate (0.4 mmol) was added. The red solution was stirred for 30 min and then evaporated to obtain a pure product (according to the NMR spectra) in a nearly quantitative yield. The solid compound was

crystallised from 4 ml of hot acetonitrile to obtain 150 mg (68 %) of **4dt** as brownish-red cubes. ^{1}H NMR and XRD analyses show that complex crystallizes as a acetonitrile adduct 2(**4dt**)·3MeCN. IR: 2956m, 1692s, 1554w, 1470s, 1445m, 1420w, 1415w, 1390w, 1361m, 1297m, 1221vs (br), 1169s, 1128m, 1093w, 1058w, 1038s, 1028m, 1008w, 952w, 914m, 874m, 856s, 804m, 777w, 759m, 690w, 666w, 652w, 615w, 583w, 554s, 484w, 464m cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.20 (2 H, d, J = 2.4 Hz, 3-H & 16-H), 6.88 (2 H, d, J = 2.4 Hz, 5-H & 14-H), 4.61 (2 H, d, J = −14.1 Hz, 7-H_{syn} & 12-H_{syn}), 4.34 (2 H, m, 2×OCH_AH$_B$), 4.33 (2 H, m, 2×OCH$_A$$H_B$), 4.29 (2 H, d, J = −14.1 Hz, 7-H_{anti} & 12-H_{anti}), 3.71 (2 H, m, 9-H_{anti} & 10-H_{anti}), 2.92 (6 H, s, N8-CH_3 & N11-CH_3), 2.68 (2 H, m, 9-H_{syn} & 10-H_{syn}), 1.32 (6 H, t, J = 7.1 Hz, 2×OCH$_2$CH_3), 1.25 (18 H, s, 4-*t*Bu & 15-*t*Bu), 1.09 (18 H, s, 2-*t*Bu & 17-*t*Bu). ^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ 172.9 (2 C, C(S)=C(S)), 166.8 (2 C, 2×C=O), 155.5 (2 C, C1 & C18), 143.3 (2 C, C4 & C15), 137.2 (C2 & C17), 124.8 (2 C, C3 & C16), 123.8 (2 C, C5 & C14), 119.2 (2 C, C6 & C13), 72.1 (2 C, C7 & C12), 61.3 (2 C, 2×OCH$_2$CH$_3$), 60.8 (2 C, C9 & C10), 53.8 (2 C, N8-CH_3 & N11-CH_3), 34.8 (2 C, 2-C(CH_3)$_3$ & 17-C(CH_3)$_3$), 34.5 (2 C, 4-C(CH_3)$_3$ & 15-C(CH_3)$_3$), 31.4 (6 C, 4-C(CH$_3$)$_3$ & 15-C(CH$_3$)$_3$), 29.9 (6 C, 2-C(CH$_3$)$_3$ & 17-C(CH$_3$)$_3$), 14.3 (2 C, 2×OCH$_2$$CH_3$).
UV/vis, λ_{max} (ε, dm^{3}mol^{-1}cm^{-1}) 310 (18900), 375 nm (7200), 510 (1010). Anal. Calcd. (%) for $C_{44}H_{60}N_2O_6S_2W$ (960.93 g/mol): C, 55.00; H, 6.29; N, 2.92. Found: C, 54.94; H, 6.37; N, 2.79

Electrochemistry

All electrochemical experiments were carried out in a conventional three-electrode one-compartment cell by using the CV technique with the potential controlled by an Autolab (PGSTAT101) potentiostat. In the CV experiments platinum, with 1 mm Ø, was used as a working electrode and a platinum wire and an Ag wire coated with AgCl were used as counter and reference electrode, respectively. The Ag/AgCl electrode was calibrated vs. ferrocene (Fe/Fe$^+$) ($E_{1/2}$ (Fe/Fe$^+$) = 0.35 V) before each experiment. The Pt electrode was polished mechanically with diamond paste (¼ to 7 µm, Struers A/s) and rinsed with deionized water before each experiment. All solutions where purged with nitrogen and experiments where performed under nitrogen at room temperature. The compounds **1dt** and **4dt** were dissolved in acetonitrile containing 0.1 M of tetrabutylammonium perchlorate ($TBAClO_4$) as a supporting electrolyte. Typically ca. 10^{-3} M solutions of the compounds were used for the CV experiments. The voltammograms were recorded at scan rates ranging from 50-200 mV/s over the potential range of 0 to 1.5 V. Dried acetonitrile was used in all electrochemical experiments. It was stored and taken in a glowbox. The electrolyte salt $TBAClO_4$ was dried at 100 °C before use.

Single Crystal X-ray diffraction

Single crystal analyses were carried out at 123 K by either a Bruker-Nonius/Kappa CCD diffractometer using Mo Kα (λ = 0.71073 Å) radiation (**1S$_2$**, **3S$_2$** and **4S$_2$**) or with a dual source (Cu/Mo) Agilent SuperNova diffractometer, equipped with Atlas CCD area-detector, using Mo Kα (λ = 0.71073 Å) radiation (**1S$_2$**, **3S$_2$** and **4S$_2$**) or with a dual source (Cu/Mo) Agilent SuperNova diffractometer using multilayer optics monochromated Cu Kα (λ = 1.54184 Å) radiation (**1dt**, **4dt**). In the former case, data collection and processing were done with programs COLLECT[35] and DENZO-SMN,[36] respectively, and semi-empirical absorption corrections were carried out with SADABS[37] whereas in the latter case CrysAlisPRO program[38] was used for data collection, processing and analytic numerical absorption correction based on a multifaceted crystal model. The crystal structures were solved with ShelXS[39] program and refined on F^2 by full matrix least squares techniques with ShelXL[39] program as implemented in WinGX[40] and Olex^2 (v.1.2.5)[41] program packages. All atoms heavier than hydrogen were refined with anisotropic displacement parameters, whereas hydrogen atoms were refined as riding atoms using isotropic displacement parameters 1.2-1.5 times of the host atoms. All figures were drawn with the program Mercury.[42] CCDC 1052251 – 1052255 contain the supplementary crystallographic data for **1dt**, **1S$_2$**, **3S$_2$**, **4dt**, and **4S$_2$** respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+ 44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

NMR spectroscopy

The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance 500 spectrometer (^{1}H: 500.13 MHz, ^{13}C: 125.76 MHz) by using deuterated chloroform ($CDCl_3$) as solvent, at 25 °C (298 K). The spectrometer was equipped with a broad-band tuneable probe (Bruker BBO-5mm-Zgrad). Both proton and carbon chemical shifts were referenced to internal tetramethylsilane (δ_{TMS} = 0.00 ppm). The 1D ^{1}H NMR spectra were measured with a single-pulse−acquire sequence (with a 30° flip angle and 5.1 s recycling delay). The 1D ^{13}C NMR spectra (with a 45° flip angle and 3.1 s recycling delay) were measured with broadband ^{1}H decoupling (waltz16). The gradient-selected ^{1}H{^{1}H} COSY spectra were recorded in a double-quantum filtered mode. ^{1}H{^{1}H} NOE spectra were acquired with the 1D DPFGSE-NOE or 2D NOESY sequences using a 0.30 s mixing time for the 2D experiments and a range of mixing times between 0.25 and 1.00 s for the 1D experiments. The ^{1}H{^{13}C} HSQC spectra were recorded with multiplicity editing (CH and CH_3 correlation signals positive, CH_2 negative) and were optimized to detect one-bond couplings with $^1J_{CH}$ = 145 Hz. The ^{1}H{^{13}C} HMBC long-range correlation experiments were optimized to detect couplings with $^nJ_{CH}$ = 8–12 Hz while the one-bond couplings around J_{CH} = 145 Hz were filtered out. The crowded ppm-regions of the ^{1}H NMR spectra were analysed with the PERCH NMR software.[43]

Acknowledgements

This work was supported by COST Action CM1003 "Biological oxidation reactions - mechanisms and design of new catalysts"

References

1 L. E. Bevers, P.-L. Hagedoorn and W. R. Hagen, *Coord. Chem. Rev*., 2009, **253,** 269.
2 (a) R. Hille, *Chem. Rev.* 1996, **96**, 2757. (b) R. Hille, *Trends Biochem. Sci*., 2002, **27**, 360.
3 C. Schulzke, *Eur. J. Inorg. Chem.* 2011, 1189.

[4] H. Sugimoto and H. Tsukube, *Chem. Soc. Rev.*, 2008, **37**, 2609.
[5] T. B. Rauchfuss, *Prog. Inorg. Chem.*, 2004, **52**, 1.
[6] A. A. Eagle, G. N. George, E. R. T. Tiekink and C. G. Young, *J. Inorg. Biochem.*, 1999, **76**, 39.
[7] S. A. Sproules, H. T. Morgan, C. J. Doonan, J. M. White and C. G. Young, *Dalton Trans*., 2005, 3552.
[8] H. Adams, M. N. Bancroft, M. J. Morris and A. E. Riddiough, *Inorg. Chem.*, 2009, **48**, 9557.
[9] K. R. Barnard, R. W. Gable and A. G. Wedd, *J. Biol. Inorg. Chem.*, 1997, **2**, 623.
[10] A. A. Eagle, E. R. T. Tiekink, G. N. George and C. G. Young, *Inorg. Chem.*, 2001, **40**, 4563.
[11] S.-B. Yu and R. H. Holm, *Inorg. Chem*., 1989, **28**, 4385−4391.
[12] K. Wieghardt, M. Hahn, J. Weiss and W. Swiridoff, *Z. Anorg. Allg. Chem.*, 1982, **492**, 164.
[13] J. W. McDonald, G. D. Friesen, L. D. Rosenhein and W. E. Newton, *Inorg. Chim. Acta,* 1983, **72**, 205.
[14] J. W. Faller and Y. Ma, *Organometallics* 1989, **8**, 609.
[15] D. V. Partyka and R. H. Holm, *Inorg. Chem*., 2004, **43**, 8609.
[16] S. Groysman, J.-J. Wang, R. Tagore, S. C. Lee and R. H. Holm, *J. Am. Chem. Soc*., 2008, **130**, 12794.
[17] S. Bristow, D. Collison, C. D. Garner and W. Clegg, *J. Chem. Soc., Dalton Tran*s., 1983, 2495.
[18] Y. Do, E. D. Simhon and R. H. Holm, *Inorg. Chem*., 1985, **24**, 1831.
[19] I. Feinstein-Jaffe, J. C. Dewan, and R. R. Schrock, *Organometallics*, 1985, **4**, 1189.
[20] W. G. Klemperer and C. Schwartz, *Inorg. Chem.*, 1985, **24**, 4459.
[21] J.-J. Wang and R. H. Holm, *Inorg. Chem*., 2007, **46**, 11156.
[22] D. V. Partyka, R. J. Staples and R. H. Holm, *Inorg. Chem.,* 2003, **42**, 7877.
[23] M. R. Pedrosa, J. Escribano, R. Aguado, R. Sanz, V. Díez and F. J. Arnáiz, *Polyhedron*, 2010, **29**, 841.
[24] (a) A. Lehtonen, M. Wasberg and R. Sillanpää, *Polyhedron*, 2006, **25**, 767. (b) A. Lehtonen, *Inorg. Chem. Commun*., 2005, **8**, 122.
[25] 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.
[26] C. J. Hinshaw, G. Peng, R. Singh, J. T. Spence, J. H. Enemark, M. Bruck, J. Kristofzski, S. L. Merbs, R. B. Ortega and P. A. Wexler, *Inorg. Chem*., 1989, **28**, 4483.
[27] J.-W. Lim, Y.-C. Park and M. Mikuriya, *Bull. Chem. Soc. Jpn*., 2002, **75**, 2011.
[28] F. Madeira, S. Barroso, S. Namorado, P. M. Reis, B. Royo and A. M. Martins, *Inorg. Chim. Acta*, 2012, **383**, 152.
[29] X. Lei and N. Chelamalla, *Acta Crystallogr*., *Sect. E: Struct. Rep. Online*, 2011, **67m**, 1510.
[30] M. Miao, M. W. Willer and R. H. Holm, *Inorg. Chem.*, 2000, **39**, 2843.
[31] R. Cao and K. Tatsumi, *Inorg. Chem.*, 2002, 41, 4102.
[32] A. Dietrich, B. Neumüller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 2000, **626**, 1837.
[33] J. Bendix, A. Bøgevig, *Inorg. Chem.*, 37, **1998**, 5992.
[34] A. L. Tenderholt, J.-J. Wang, R. K. Szilagyi, R. H., Holm, K. O., Hodgson, B. Hedman and E. I. Solomon, *J. Am. Chem. Soc*., 2010, **132**, 8359.
[35] COLLECT, Bruker AXS, Inc.: Madison, WI, 2008.
[36] Z. Otwinowski and W. Minor, *Methods Enzymol*., 1997, **276**, 307.
[37] G. M. Sheldrick, SADABS; University of Göttingen: Göttingen, Germany, 2012.
[38] CrysAlis^{Pro} program, version 1.171.37.31, Agilent Technologies, Oxford, 2012.
[39] G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.
[40] L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.
[41] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. J. Puschmann, *Appl. Cryst.*, 2009, **42**, 339.
[42] Mercury CSD 2.0 - New Features for the Visualization and Investigation of Crystal Structures, C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Cryst.*, 2008, **41**, 466.
[43] R. Laatikainen, M. Niemitz, U. Weber, J. Sundelin, T. Hassinen and J. Vepsäläinen, *J. Magn. Reson., Ser. A*, 1996, **120**, 1. Software homepage: http://www.perchsolutions.com.

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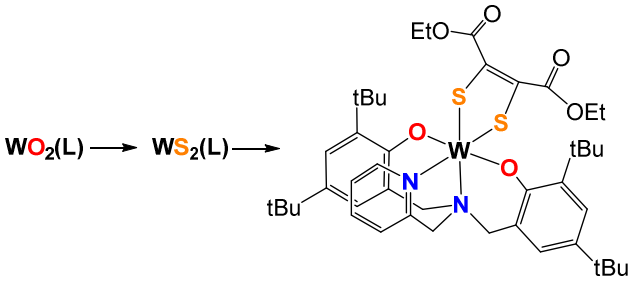
Table 2. Summary of crystallographic data for studied compounds at 123 K.

Complex	**1S$_2$**	**3S$_2$**	**4S$_2$**	**1dt**	**4dt**
Formula	$C_{36}H_{50}N_2O_2S_2W$	$C_{33}H_{51}NO_3S_2W{\cdot}CH_2Cl_2$	$C_{34}H_{54}N_2O_2S_2W$	$C_{44}H_{60}N_2O_6S_2W$	$2(C_{42}H_{64}N_2O_6S_2W){\cdot}3(C_2H_3N)$
M_r	790.75	842.64	770.76	960.91	2005.00
Crystal system	triclinic	orthorhombic	monoclinic	orthorhombic	monoclinic
Space group (no.)	P-1 (2)	Pbca (61)	$P2_1/c$ (14)	$P2_12_12_1$ (19)	$P2_1/c$ (14)
a/Å	13.4235(3)	14.9889(2)	18.1922(3)	10.06798(12)	16.18664(9)
b/Å	15.4757(4)	17.3185(3)	15.1933(2)	16.8748(2)	34.93266(18)
c/Å	21.8073(5)	28.4713(4)	25.7879(4)	26.8615	18.54984(10)
α/°	70.9770(10)	90	90	90	90
β/°	78.0260(10)	90	96.0760(10)	90	113.6854(6)
δ/°	67.0300(10)	90	90	90	90
V/Å^3	3926.41(17)	7390.73(19)	7087.72(19)	4563.64(10)	9605.33(10)
Z	4	8	8	4	4
μ/mm^{-1}	3.078[a]	3.416[a]	3.408[a]	5.908[b]	5.644[b]
Obs. reflections	15389	8024	15430	7997	17072
R_{int}	0.0353	0.0342	0.032	0.0239	0.0185
Parameters	799	401	798	510	1133
R1[c]	0.045 (0.033)[d]	0.0273(0.0405)	0.0271 (0.0352)	0.0232 (0.0241)	0.0233 (0.0254)
wR2[e]	0.0775 (0.0727)	0.0527 (0.0489)	0.056 (0.0584)	0.0599 (0.0604)	0.0552 (0.0563)
Goodness of fit	1.022	1.056	1.059	1.028	1.035
Peak, hole */e Å^{-3}*	0.818, -1.306	0.608, -0.642	0.727, -0.815	0.511, -0.696	0.605, -0.845

[a] MoK_α radiation
[b] CuK_α radiation
[c] $R1 = \Sigma \, | \, |Fo| - |F_c| \, | \, / \, \Sigma \, |F_o|$
[d] values in parentheses for reflections with $I > 2.0\sigma(I)$
[e] $wR2 = \{ \, \Sigma \, [\, w(F_o^2 - F_c^2)^2 \,] \, / \, \Sigma \, [\, w(F_o^2)^2 \,] \, \}^{1/2}$ and
$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP)]$, where $P = (2F_c^2 + F_o^2)/3$

Table of contents entry:



Dioxotungsten(VI) complexes react with thionation reagents to form disulphides and furthermore with activated alkyne to generate dithiolene complexes.