This article is published as part of the Dalton Transactions themed issue entitled:

Dalton Transactions 40th Anniversary

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Published in issue 40, 2011 of Dalton Transactions



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Dalton Transactions

Cite this: Dalton Trans., 2011, 40, 10457

PAPER

Synthesis, structure and redox properties of bis(cyclopentadienyl)dithiolene complexes of molybdenum and tungsten[†]

Alexandra L. Whalley,^{*a*} Alexander J. Blake,^{*a*} David Collison,^{*b*} E. Stephen Davies,^{*a*} Helen J. Disley,^{*a*} Madeleine Helliwell,^{*b*} Frank E. Mabbs,^{*b*} Jonathan McMaster,^{*a*} Claire Wilson^{*a*} and C. David Garner^{**a*}

Received 14th April 2011, Accepted 2nd June 2011 DOI: 10.1039/c1dt10663e

The compounds $[Cp_2M(S_2C_2(H)R)]$ (M = Mo or W; R = phenyl, pyridin-2-yl, pyridin-3-yl, pyridin-4-yl or quinoxalin-2-yl) and $[Cp_2Mo(S_2C_2(Me)(pyridin-2-yl)]$ have been prepared by a facile and general route for the synthesis of dithiolene complexes, viz. the reaction of $[Cp_2MCl_2]$ (M = Mo or W) with the dithiolene pro-ligand generated by reacting the corresponding 4-(R)-1,3-dithiol-2-one with CsOH. These Mo compounds were reported previously (Hsu et al., Inorg. Chem. 1996, 35, 4743); however, the preparative method employed herein is more versatile and generates the compounds in good yield and all of the W compounds are new. Electrochemical investigations have shown that each compound undergoes a diffusion controlled one-electron oxidation (OX1) and a one-electron reduction (RED1) process; each redox change occurs at a more positive potential for a Mo compound than for its W counterpart. The mono-cations generated by chemical or electrochemical oxidation are stable and the structures of both components of the $[Cp_2Mo(S_2C_2(H)R)]^+/[Cp_2Mo(S_2C_2(H)R)]$ (R = Ph or pyridin-3-yl) redox couples have been determined by X-ray crystallography. For each redox related pair, the changes in the Mo-S, S-C and C-C bond lengths of the {MoSCCS} moiety are generally consistent with OX^I involving the loss of an electron from a π -orbital that is Mo–S and C–S antibonding and C–C bonding in character. These results have been interpreted successfully within the framework provided by DFT calculations accomplished for $[Cp_2M(S_2C_2(H)Ph)]^n$ (M = Mo or W; n = +1, 0 or -1). The HOMO of the neutral compounds is derived mainly from the dithiolene π_3 orbital (65%); therefore, OX^{1} is essentially a dithiolene-based process. The similarity of the potentials for OX^{1} (ca. 30 mV) for analogous Mo and W compounds is consistent with this interpretation and the EPR spectra of each of the Mo cations show that the unpaired electron is coupled to the dithiolene proton but relatively weakly to ^{95,97}Mo. The DFT calculations indicate that the unpaired electron is more localised on the metal in the mono-anions than in the mono-cations. In agreement with this, the EPR spectrum of each of the Mo-containing mono-anions manifests a larger 95,97 Mo coupling (A_{iso}) than observed for the corresponding mono-cation and RED¹ for a W compound is significantly (ca. 300 mV) more negative than that of its Mo counterpart. $[Cp_2W(S_2C_2(H)(quinoxalin-2-yl))]$ is anomalous; RED¹ occurs at a potential ca. 230 mV more positive than expected from that of its Mo counterpart and the EPR spectrum of the mono-anion is typical of an organic radical. DFT calculations indicate that these properties arise because the electron is added to a quinoxalin-2-yl π -orbital.

Introduction

Transition metal complexes containing one, two or three dithiolene ligands have attracted a sustained interest since the 1960s, given their versatile redox behaviour, novel electronic and molecular structures, and strategically valuable applications, including their potential use as tunable near-IR dyes and conducting materials.¹⁻³ The dithiolene group also plays a vital role in the majority of living systems as the component of the molybdopterin (MPT) co-factor that coordinates the metal at the catalytic centre of Mo-and W-oxotransferase enzymes⁴ and is essential for their catalytic action.⁵ Therefore, the synthesis^{2.6} of new dithiolene complexes represents valuable new chemistry and investigations of their electronic structure,⁷ properties³ and reactions.⁸

Metal dithiolene complexes with 1:1, 1:2 or 1:3 metal:ligand stoichiometry have been investigated extensively;^{1,2} complexes with a 1:1 stoichiometry allow the effects of a redox change localised

^aSchool of Chemistry, The University of Nottingham, University Park, Nottingham, UK, NG7 2RD. E-mail: dave.garner@nottingham.ac.uk; Fax: +44 0115 951 3563; Tel: +44 0115 951 4188

^bSchool of Chemistry, The University of Manchester, Oxford Road, Manchester, UK, M13 9PL

[†] Electronic supplementary information (ESI) available. CCDC reference numbers 822493–822498. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10663e

on a single metalladithiolene moiety to be studied.³ In this latter respect, the η^5 -cyclopentadienyl group restricts the coordination sites available for dithiolene binding and compounds such as [CpM(dithiolene)] (M = Co, Rh, Ir, or Ni) and $[Cp_2M(dithiolene)]$ (Ti, V, Mo, W, Zr, Hf, or Nb) have been isolated.³ Also, we have reported the synthesis of a range of [CpCo(dithiolene)] compounds,⁹⁻¹² the reversible redox chemistry of which is limited to a one-electron reduction. In contrast, $[Cp_2M(dithiolene)]$ (M = Mo or W) compounds can undergo two reversible oxidations and some of the mono-cationic products have been characterised by X-ray crystallography.¹³⁻¹⁷ The information obtained shows that the one-electron oxidation of a $[Cp_2M(dithiolene)]$ (M = Mo or W) compound leads to a decrease in the length of the C-S bonds and an increase in the length of the C-C bond within the metal-dithiolene unit (i.e. the dithiolene moiety possesses more dithioketonic character in the mono-cation than in the neutral compound); these changes are consistent with the results of Density Functional Theory (DFT) calculations which indicate that the frontier molecular orbital is essentially localised on the dithiolene.17

An important aspect of the structure of [Cp₂M(dithiolene)] compounds is the extent of the folding of the {MSCCS} metallacycle along the S–S axis (θ); compounds with a d^0 configuration are folded to a significant extent ($40^{\circ} < \theta < 50^{\circ}$) whereas those with a d^2 configuration are essentially planar ($\theta \sim 0^\circ$). Lauher and Hoffmann¹⁸ used extended Hückel calculations and explained these observations in terms of metal-dithiolene π -bonding and the d-orbital occupancy of the metal. The results of subsequent studies of the electronic structure of these compounds, including gasphase photoelectron spectroscopic studies and DFT calculations accomplished for $[Cp_2Ti(bdt)]$ and $[Cp_2Mo(bdt)]$ (bdt = 1,2benzenedithiolate),¹⁹ are consistent with this view and highlight the interaction of metal in-plane and sulfur π orbitals. An interesting refinement of this situation is the observed variation in the value of θ for the d^1 complex, $[Cp_2Mo(dmit)]^+$ (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate) with the nature of the anion: $\theta \sim 0^{\circ}$ for the $[PF_6]^-$, $[AsF_6]^-$ and $[SbF_6]^-$ salts, 23.2° for the $[BF_4]^-$ salt and 30.5° for the Br⁻ salt.¹⁶ DFT calculations show that the variation in the value of θ observed for $[Cp_2Mo(dmit)]^+$ is a consequence of the very low energy barrier (<1 kcal mol⁻¹) for folding along the S-S axis of this complex.¹⁷

Following the synthesis and structural characterisation of $[Cp_2Mo(S_2C_2(C(O)Me)(quinoxalin-2-yl))]^{20}$ Hsu *et al.* reported the synthesis of $[Cp_2Mo(S_2C_2(R)Ar)]$ (R = H, Ar = quinoxalin-2-yl, pyridin-2, 3 or 4-yl, Ph, 4-chlorophenyl or pyrenyl; R = Me, Ar = quinoxalin-2-yl; or Ar = R = Ph).²¹ UV/vis, ¹H NMR and IR properties of these compounds were recorded and electrochemical studies showed that each undergoes a reversible one-electron oxidation, the potential of which depends upon the nature of the Ar and R groups. Also, Hsu *et al.* showed that $[Cp_2Mo(S_2C_2(R)Ar)]$ (R = H, Ar = quinoxalin-2-yl, pyridin-2, 3, or 4-yl; R = Me, Ar = quinoxalin-2-yl) undergo a reversible protonation. X-ray crystallographic studies showed that $[Cp_2Mo(S_2C_2(quinoxalin-2-yl))]$ possesses a planar metallo-1,2-enedithiolate group whereas in its protonated derivative (as the $[BF_4]$ salt) the Mo is 0.344(10) Å out of the plane of the ene-1,2-dithiolate unit.²⁰

The aim of this study is to compare and contrast the nature and properties, notably the redox characteristics and electronic structure, of analogous compounds of molybdenum and tungsten that contain one of the dithiolene ligands $S_2C_2(H)R$ (R = phenyl, pyridin-2-yl, pyridin-3-yl, pyridin-4-yl or quinoxalin-2-yl). These investigations have led to the development of a new synthetic route to these $[Cp_2M(S_2C_2(H)R)]$ (M = Mo or W) compounds and their characterisation by ¹H and ¹³C NMR spectroscopies. Electrochemical and associated UV/vis/NIR spectro-electrochemical studies have demonstrated the redox versatility of these compounds and the structures of both constituents of $[Cp_2Mo(S_2C_2(H)R)]^+/[Cp_2Mo(S_2C_2(H)R)]$ (R = Ph and pyridin-3-yl) redox couples have been determined by X-ray crystallography. X-band Electron Paramagnetic Resonance (EPR) spectra have been recorded for the mono-cations and mono-anions and DFT calculations have provided valuable insights into the electronic structure of selected neutral compounds and the corresponding mono-cation and mono-anion.

Results and discussion

Synthesis

The compounds **1** to **10**, $[Cp_2M(S_2C_2(H)R] (M = Mo \text{ or } W; R = phenyl, pyridin-2-yl, pyridin-3-yl, pyridin-4-yl or quinoxalin-2-yl) have been synthesised in good (Mo; 44 to 71%) or moderate (W; 15 to 35%) yield by hydrolysis of the appropriate 4-(R)-1,3-dithiol-2-one with CsOH to release the corresponding ene-1,2-dithiolate for metathesis with <math>[Cp_2MCl_2] (M = Mo \text{ or } W)$ (Scheme 1). Compound **11**, $[Cp_2Mo(S_2C_2(Me)(pyridin-2-yl)]$, was synthesised in an analogous manner using 4-(pyridin-2-yl)-5-(methyl)-1,3-dithiol-2-one. Given that the hydrolysed ligand precursors are sensitive to decomposition, the lower yields for W compounds may reflect the longer reaction times that are required for their formation. The synthesis of these $[Cp_2W(S_2C_2(H)R]$ compounds has not been reported previously and, although the majority of $[Cp_2Mo(S_2C_2(H)R]]$ were reported by Hsu *et al.*,²¹ the synthetic procedure described herein generally leads to higher yields.

NMR Spectroscopy

The ¹H and ¹³C NMR spectra recorded for 1 to 10 are consistent with the structure of $[Cp_2Mo(S_2C_2(H)R]]$ compounds depicted in Scheme 1, as confirmed by our X-ray crystallographic studies of 3, 7 and 9 (vide infra) and that of 5 accomplished by Hsu et al.²¹ The ¹H NMR spectra of 1 to 10 at ambient temperature in $CDCl_{\scriptscriptstyle 3}$ contain a single, sharp resonance for the $\eta^{\scriptscriptstyle 5}\text{-}Cp$ protons (at 5.22-5.35 ppm, cf. 5.25-5.29 ppm for 1 to 5²¹) consistent with the absence of processes involving either the bending of the dithiolene ligand about the S-S axis or a dynamic inversion.²⁴ The chemical shifts for the dithiolene ¹H resonance (6.30-7.82 ppm for 1 to 10) are consistent with the dithiolene ligand having ene-1,2-dithiolate character,^{25,26} in agreement with the results of our DFT calculations (vide infra) and theoretical studies of related compounds.^{17,18} The relative chemical shift of the dithiolene ¹H NMR resonance for each $[Cp_2M(S_2C_2(H)R] (M = Mo \text{ or } W)$ series correlates with the nature of the other dithiolene substituent as: R = quinoxalin-2-yl > pyridin-2-yl > pyridin-4-yl > pyridin-3-yl > phenyl. This sequence corresponds to that observed for the ¹H NMR resonance for $[MO(dithiolene)_2]^{2-}$ (M = Mo or W) complexes involving the same set of dithiolene ligands. This order has been rationalised on the basis of inductive effects and the



relative ability of the R group to stabilise a resonance form in which positive charge is localised at the carbon atom bound to the dithiolene proton.²² The chemical shift of the dithiolene proton of each of the W compounds is *ca*. 0.4 ppm more shielded than that of the analogous Mo compound and possesses a pair of satellite peaks with ³J values of 9.6–10.6 Hz that are attributed to the coupling of the dithiolene proton with ¹⁸³W (abundance 14.6%). The ³J values observed are comparable to those reported for [W{S₂C₂(H)(C₆H₄OMe-p)}₃] (*J*=10.5 Hz)²⁷ and [WO(qedt)₂]^{2–} (*J*=10.2 Hz).²³

Electrochemical and spectroelectrochemical investigations

Cyclic voltammetric studies of compounds 1 to 10, at ambient temperature in dmf containing [" Bu_4N][BF_4] (0.2 M) as the supporting electrolyte, have shown that each compound can be oxidised and reduced (Table 1). As a typical example, the cyclic voltammetric response for 1 is shown in Fig. 1; Fig. S1 and S2 show cyclic voltammograms recorded for 2 and 6, respectively.† The changes in the UV/vis spectroscopic profiles were recorded for the oxidation of each of the compounds 1 to 10 to their monocation (OX¹) and the reduction of each of the compounds 1 to 5 and 10 to their mono-anion (RED¹). Also, our NIR spectra were recorded for the formation of selected pairs of analogous mono-cations, *viz.* [1]⁺ and [6]⁺, [3]⁺ and [8]⁺, and [5]⁺ and [10]⁺. The values of λ_{max} and ε for the absorptions observed for these mono-cations and mono-anions are summarised in Table 2 and the spectroscopic profiles for the conversion of [1] to [1]⁺ and that of [1] to [1]⁻ are presented in Fig. 2 and 3, respectively; changes observed in the spectroscopic profiles for other electrochemical conversions are shown in Fig. S3–S11.

Our electrochemical studies show that the $[Cp_2M(dithio-lene)]^+/[Cp_2M(dithiolene)]$ couple (OX¹) of each of the compounds **1** to **10** is reversible over the scan rates of 20 to 300 mVs⁻¹, in agreement with the cyclic voltammetric studies of **1** to **5** in CH₂Cl₂ accomplished by Hsu *et al.*²¹ Also, spectroelectrochemical studies show that OX¹ is chemically reversible for **1** to **3**, **5** to **8**, and **10** since, for each compound, oxidation and subsequent reduction regenerated the original spectrum. However, for **4** and **9** this redox cycle produced a UV/vis spectrum with the same profile as that of the parent compound, but with a slight variation in the band intensities.

For a given metal, the potential of the first oxidation (OX¹, see Table 1) varies with the nature of the dithiolene substituent as: R = quinoxalin-2-yl > pyridin-4-yl > pyridin-3-yl > pyridin-2-yl > phenyl; this sequence corresponds to that previously observedfor OX¹ of [MO(dithiolene)₂]²⁻ (M = Mo or W) complexes of thesedithiolene ligands.^{22,23} The E_{1/2} values for OX¹ of 1 to 5 and 6 to10 in dmf (Table 1) show a linear correlation with the Hammett

 Table 1
 Cyclic voltammetric data for compounds 1 to 10^e

Complex	$E_{1/2} \ OX^{I}/V$	$E_{p}{}^{a} \ OX^{\rm II}/V$	$E_{1/2} \ OX^{III}/V$	E _{1/2} RED ^I /V	$E_{p}{}^{c} RED^{II}/V$	$E_p^{\ c} RED^{III}/V$	$\Delta E (\mathrm{Fc^{+}/Fc})/\mathrm{V}$
1	-0.33 (0.07)	0.34	_	-2.16 (0.07)	_	_	(0.07)
2	-0.28 (0.07)	0.39	-0.12(0.07)	-2.14(0.07)	-2.63	-2.79	(0.07)
3	-0.27 (0.07)	0.37	-0.18 (0.08)	-2.13(0.07)	-2.61	-2.78	(0.07)
4	-0.23 (0.07)	0.44	-0.06 (0.07)	-2.12(0.07)	-2.59	-2.74	(0.07)
5	-0.20 (0.07)	0.44	-0.17 (0.07)	-2.10(0.07)	-2.29	_	(0.07)
6	-0.35 (0.07)	0.21 (0.08)		-2.45(0.08)			(0.08)
7	-0.31 (0.07)	0.29	-0.17 (0.07)	-2.44(0.08)	-2.65		(0.08)
8	-0.30 (0.07)	0.29	-0.22 (0.07)	-2.43(0.08)	-2.64		(0.08)
9	-0.26 (0.07)	0.36	-0.11 (0.07)	-2.42 (0.07)	-2.62	-2.81	(0.07)
10	-0.24 (0.07)	0.35	-0.22 (0.07)	-2.17 (0.07)	-2.48	-2.69	(0.07)

^{*a*} Potentials ($E_{1/2} = (E_p^a + E_p^c)/2$) in V are quoted to the nearest 0.01 V. Data reported at 0.1 V s⁻¹ for 1 mM test solutions in dmf containing 0.2 M [^{*n*}Bu₄N][BF₄] as the supporting electrolyte. The anodic/cathodic peak separation ($\Delta E = E_p^a - E_p^c$) is given in brackets where applicable. OX^{II} are E_p^a values except for **6**. RED^{II} and RED^{III} are E_p^c values. OX^{III} results from the application of a potential > OX^{II}. ΔE for the Fc⁺/Fc was used as the internal standard.

Table 2 Bands observed in the UV/vis/NIR spectra recorded for 1 to 10, $[1]^+$ to $[10]^+$, $[1]^-$ to $[5]^-$ and $[10]^-$ at 273 K in dmf containing ["Bu₄N][BF₄] (0.2 M) using an optically transparent electrode

	$[M]\lambda_{max}/nm(\epsilon \times 10^{3}/mol^{1}dm^3cm^{1})$	$[M]^{*} \; \lambda_{max} / nm \; (\epsilon \times 10^{-3} / mol^{-1} \; dm^{3} \; cm^{-1})$	$[M]^{-} \lambda_{max}/nm (\epsilon \times 10^{-3}/mol^{-1} dm^{3} cm^{-1})$
1	364 (7.3), 547 (1.8)	418 sh (4.4), 447 (4.8), 484 sh (4.1), 657 (1.5), 1149 (1.1)	291 (19.0), 349 (8.6), 427 sh (3.7), 571 (3.2)
2	383 (5.0), 529 sh (1.5)	434 (3.5), 647 (1.0)	300 (16.7), 364 (6.8), 445 sh (3.5), 565 (2.6)
3	375 (5.4), 519 (1.5)	412 sh (3.3), 446 (3.6), 653 (1.1), 1142 (1.3)	294 (15.3), 361 (6.3), 429 sh (3.3), 557 (2.7)
4	387 (7.4), 426 sh (4.9), 524 sh (2.2)	406 sh (4.2), 442 (4.4), 633 (1.6)	301(18.9), 377 (7.7), 444 (5.0), 559 (4.1)
5	327 (15.4), 517 (8.9)	321 (11.7), 370 sh (5.9), 474 (7.2), 652 (1.9), 1142 (1.1)	346 (16.7), 559 (6.8)
6	336 (6.0), 390 sh (4.6)	365 (3.5), 461 (4.1), 625 (1.6), 1046 (1.4)	
7	332 (5.5), 409 (4.8)	370 sh (3.6), 454 (3.2), 623 (1.2)	
8	348 (5.1), 397 (4.9)	361 sh (3.4), 454 (3.4), 625 (1.2), 1030 (1.2)	
9	356 (4.8), 418 (6.6)	358 sh (3.8), 445 (3.6), 616 (1.5)	
10	325 (15.5), 510 (8.3)	322 (10.0), 370 (7.2), 463 (5.7), 636 (2.0), 1046 (1.7)	321 (17.7), 451 (5.5), 586(4.8), ~650 sh (3.0)



Fig. 1 Cyclic voltammetric response of $[Cp_2Mo(sdt)](1)(1 \text{ mmol})$ in dmf containing $["Bu_4N][BF_4](0.2 \text{ M})$ at ambient temperature and a scan rate of 0.1 V s⁻¹. The dashed line shows expansion of the potential range to include OX^{II}.

parameter (σ_p) of R²⁸ with quinoxalin-2-yl being the most electron withdrawing of the substituents ($\sigma_p ca. 0.55$). Each W compound is slightly (*ca.* 30 mV) more easily oxidised than its Mo counterpart; similar observations have been made for other [Cp₂M(dithiolene)] compounds (M = Mo or W, dithiolene = dmit (2-thioxo-1,3dithiole-4,5-dithiolate), dmid (2-oxo-1,3-dithiole-4,5-dithiolate (-2)) or dddt (5,6-dihydro-1,4-dithiine-2,3-dithiolate)).¹³⁻¹⁵

Protonation of compounds 2 to 5 and 7 to 10 in dmf by the addition of >4 equivalents of *p*-toluene sulfonic acid, results in a positive shift in the value of $E_{1/2}$ for OX¹. The magnitude of this shift is similar for the Mo and W series of compounds (0.18, 0.11, 0.15 and 0.06 V for 2 to 5, respectively; 0.18, 0.10, 0.15 and 0.04 V for 7 to 10, respectively) and correlates with the p K_a of R, as observed by Hsu *et al.* for 2 to 5 in MeCN.²¹

Compounds 1 to 10 undergo a second oxidation (OX^{II}, Table 1) that is chemically irreversible in dmf at ambient temperature; each W compound is more easily oxidised (by *ca*. 100 mV) than its Mo counterpart (Table 1). For 2 to 5 and 7 to 10 significant changes were observed in the shape of the voltammogram generated when the potential was held at, or slightly above, OX^{II} (that for 2 is



Fig. 2 Changes in the UV/vis/NIR spectroscopic profile observed for the electrochemical conversion of $[Cp_2Mo(sdt)]$ ([1]) to [1]⁺ in dmf containing [^{*n*}Bu₄N][BF₄] (0.2 M) at 273 K.



Fig. 3 Changes in the UV/vis spectroscopic profile observed for the electrochemical conversion of $[Cp_2Mo(sdt)]$ ([1]) to [1]⁻ in dmf containing ["Bu₄N][BF₄] (0.2 M) at 273 K.

shown in Fig. S1†). These changes involved the depletion of the OX^{I} redox couple and the generation of a new redox couple (OX^{III}) with an $E_{1/2}$ value slightly more positive than that of

OX¹ for the parent compound (Table 1). These electrochemical results are consistent with a mechanism for the formation of OXIII from OX^{II} that involves electron transfer coupled to a chemical reaction, as reported for the oxidation of $[Cp_2Mo(SR)_2]$ (R = Me or Ph).²⁹ We have not investigated the nature of any of the products formed. In contrast, scanning through OX^{II} for 1 and 6 did not significantly perturb the current response for OX¹ in the reverse sweep of the cyclic voltammogram (for 1 see Fig. 1 and for 6 see Fig. S2[†]). For 6, at a scan rate between 100 and 300 mV s⁻¹, a return (reduction) wave was associated with the second oxidation suggesting an electrochemical reversibility for OX^{II} of this compound, *i.e.* the existence of a $[6]^{2+}/[6]^+$ couple, as reported for $[Cp_2M(dithiolene)]$ (M = Mo or W; dithiolene = dmit, dmid, dddt)^{13,14} and [Cp₂Mo(S₂C₂S(CH₂CH₂O)₃CH₂CH₂S)].³⁰ However, spectroelectrochemical studies showed that $[6]^{2+}$ is chemically unstable. Similar observations of a return (reduction) wave associated with OX^{II} were noted in the cyclic voltammograms recorded for 1, 7 and 10, but each of these oxidation products was more transient than $[6]^{2+}$ and was only observed at fast scan rates.

Compounds 1 to 10 are capable of undergoing at least one reduction process (Table 1 and *e.g.* Fig. 1), as observed for $[Cp_2Mo(dithiolene)]$ (dithiolene = dmid or dmit),¹³ with RED¹ being electrochemically reversible in each case. UV/vis spectroelectrochemical studies showed that RED¹ is chemically reversible for 1 to 5 and 10, since one-electron reduction and subsequent re-oxidation regenerated the original spectrum, but this was not the case not for 6, 7 and 8. For 1 to 9, the $E_{1/2}$ value of the first reduction (RED¹) correlates with the Hammett parameter, σ_p , of the dithiolene substituent (R).²⁸ However, 10 is reduced at a potential that is significantly less negative than expected, given the electron withdrawing nature of the quinoxalinyl substituent and the value of RED¹ for 5.

Each of the compounds 2 to 5 and 7 to 10 is capable of undergoing one or two further reductions (Table 1); however, in no case was an associated return wave observed and the products of these reductions were not investigated further.

Structural studies

The facile one-electron oxidation of the $[Cp_2M(dithiolene)]$ compounds 1 to 10 achieved electrochemically has been achieved chemically by oxidation of the parent compound with $[Cp_2Fe][BF_4]$, thereby providing a convenient route to products such as [1][BF₄], [3][BF₄] and [8][BF₄]. The structures of 1, [1][BF₄], 3, [3][BF₄], [8][BF₄] and 9 have been determined by X-ray crystallography (Fig. 4). In each case, the geometry at the metal centre can be considered to approximate to that of a distorted tetrahedron, with the vertices comprising the centroids of the two Cp rings and the two dithiolene sulfur atoms. The {MSCCS} metallacycle is not coplanar with the R group of the dithiolene, but there is a shift toward co-planarity upon oxidation.³¹

The bond lengths and interbond angles of the {MoSCCS} metallacycle of $[Cp_2Mo(dithiolene)]^n$ (n = 0 or +1) are summarised in Table 3 where it is evident that the asymmetric nature of each dithiolene ligand can give rise to different Mo–S and S–C bond lengths within each metallacycle. A similar effect is noted for W-containing [8][BF₄] and 9. For 1, 3 and 9, the lengths of the M–S, S–C and C–C bonds and the values of the interbond angles are similar to those of other structurally characterised

[Cp₂Mo(dithiolene)] compounds.^{20,31-33} Oxidation of **1** and **3** to the mono-cation results in a decrease in the length of the Mo–S bond (by 0.013–0.041 Å) and S–C bonds (by 0.042–0.080 Å); oxidation leads to an increase in the length of the C–C bond of **1** (by *ca*. 0.43 Å) and **3** (by *ca*. 0.34 Å).

The {MoSCCS} metallacycle of **1** and **3** is planar with a mean deviation of the atoms from the plane of <0.01 Å. The {WSCCS} metallacycle of **9** is folded by 7.72(8)° about the S–S axis, which is close to the value of 8.1° in [Cp₂W(bdt)] (bdt = 1,2-benzenedithiolate).³² The lack of a major fold about the S–S axis for these compounds is consistent with the structures of other [Cp₂Mo(dithiolene)] compounds^{13,17,20,32–34} and theoretical considerations of the electronic structure of [Cp₂M(dithiolene)] (M = Mo or W) compounds¹⁸ that (formally) involve a metal centre with a d^2 configuration. In each cation, the {MSCCS} metallacycle is folded at the S–S axis, by 7.79(16)° for [**1**]⁺, 23.73(17)° for [**3**]⁺, and 29.03(3)° for [**8**]⁺.

The substitution of W for Mo in $[Cp_2M(3-pedt)]^+$ (compounds $[3]^+$ and $[8]^+$, respectively) does not result in major change in the bond distances and interbond angles within the {MSCCS} metallacycle.

EPR spectroscopic studies

The EPR spectra of $[1]^*$ to $[11]^*$ were recorded at X-band frequency. These cations were produced by *in situ* electrochemical oxidation of the parent compound in dmf containing ["Bu₄N][BF₄] (0.2 M) or by oxidation of the corresponding parent compound in CH₂Cl₂ solution by *ca*. one equivalent of [Cp₂Fe][BF₄]. Details of the EPR spectra recorded at 273 K in dmf and 210 and 77 K in CH₂Cl₂ are summarised in Table 4 and illustrated in Fig. 5 to 8 and S12 to S16.[†]

The EPR spectrum of each chemically generated Mo-containing cation ([1]+ to [4]+ and [11]+) in CH₂Cl₂ at 273 K was an unresolved singlet. Optimum resolution of the fluid solution EPR spectra for these cations was obtained in CH₂Cl₂:dmf (4:1 v/v) at ca. 210 K (e.g. see Fig. 5(a)); at this temperature six 95,97 Mo (I = 5/2) satellites were observed superimposed on the 92,94,96,98,100 Mo (I = 0) signal. Also manifest in the EPR spectra of $[1]^+$ to $[4]^+$ in CH₂Cl₂:dmf (4:1 v/v) at *ca.* 210 K was a further splitting that is attributed to the coupling of the unpaired electron spin with the magnetic moment of a unique proton, presumably the dithiolene proton. Samples of $[1]^+$, $[3]^+$, and $[5]^+$, prepared by *in situ* electrochemical oxidation of the parent compound in dmf containing ["Bu₄N][BF₄] (0.2 M), each gave a well resolved fluid solution EPR spectrum at 273 K; metal and ligand (dithiolene) hyperfine structure was evident in the spectra of $[1]^+$ (see Fig. S12⁺), $[3]^+$ and $[5]^+$, and this was consistent with the EPR spectra recorded for samples generated by chemical oxidation. In [11]⁺ the dithiolene proton of $[2]^+$ is replaced by a methyl group; in addition to the coupling with ^{95,97}Mo; the EPR spectrum of [11]⁺ [see Fig. 5(b)] manifests hyperfine splitting consistent with the coupling of the unpaired electron spin with the magnetic moment of three equivalent protons, presumably those of the methyl group.

For the W-containing cations, whether generated electrochemically in dmf ([6]⁺ and [10]⁺) or chemically in CH₂Cl₂ ([6]⁺ to [9]⁺), at 273 K each EPR spectrum comprises two ¹⁸³W (I = 1/2) satellites superimposed on a single line ^{180,182,184,186}W (I = 0), *e.g.* Fig. 6. The EPR spectrum recorded for each of the cations [1]⁺ (Fig. S13⁺)



C5C

C4C

[8][BF₄]

Fig. 4 Molecular structures of $[Cp_2Mo(sdt)](1)$, $[1][BF_4]$, $[Cp_2Mo(3-pedt)](3)$, $[3][BF_4]$, $[Cp_2W(3-pedt)][BF_4]$ ($[8][BF_4]$) and $[Cp_2W(3-pedt)](9)$; hydrogen atoms and anions are omitted for clarity.

to $[4]^+$, $[6]^+$ (Fig. S14[†]) to $[9]^+$ and $[11]^+$, prepared by chemical oxidation in CH₂Cl₂:dmf (4:1, v/v), as a frozen (77 K) solution was rhombic and showed no clearly resolved metal hyperfine structure. Within experimental error, the g_{ave} ($-g_{iso}$) value observed for each cation was the same for the frozen and the fluid solutions, implying that no major structural changes occur between these phases.

The *in situ* electrochemical production of $[1]^-$, $[3]^-$ and $[5]^-$ in dmf at 273 K allowed their EPR spectra to be recorded; details of these spectra are given in Table 4 and the spectra of $[1]^-$ and $[3]^-$ are shown in Fig. 7 and S15,† respectively. Each spectrum comprises six ^{95,97}Mo (I = 5/2) satellites superimposed on the single line ^{92,94,96,98,100}Mo (I = 0) with A_{iso} ca. 40 G. No ligand hyperfine coupling was observed but this may be concealed since the line

9

C7C

C6

C80

S1

C1

Table 3 Selected bond lengths (Å) and interbond angles (°) for 1, [1][BF₄], 3, [3][BF₄], [8][BF₄] and 9

Complex	1	1 [BF ₄]	3	$3[BF_4]$	8 [BF ₄]	9
Bond lengths/Å						
M-S(1)	2.4402(7)	2.413(2)	2.4506(15)	2.4097(12)	2.397(3)	2.4446(7)
M-S(2)	2.4396(7)	2.425(2)	2.4375(15)	2.4240(12)	2.404(3)	2.4326(8)
S(1) - C(1)	1.746(3)	1.666(5)	1.728(6)	1.688(5)	1.694(10)	1.743(3)
S(2) - C(2)	1.771(3)	1.714(5)	1.771(5)	1.730(4)	1.726(9)	1.769(3)
C(1) - C(2)	1.327(3)	1.370(7)	1.339(8)	1.367(7)	1.353(13)	1.355(4)
Interbond angles/°						
S(1)-M-S(2)	82.29(2)	81.77(4)	82.30(5)	81.41(4)	81.34(9)	82.13(2)
M - S(1) - C(1)	106.06(9)	106.14(17)	105.8(2)	104.08(16)	103.3(3)	106.42(9)
M - S(2) - C(2)	106.85(8)	107.07(17)	106.9(2)	104.42(16)	103.2(4)	107.19(10)
S(1) - C(1) - C(2)	124.2(2)	125.3(4)	125.0(4)	124.4(4)	123.3(8)	123.2(2)
S(2) - C(2) - C(1)	120.5(2)	119.0(4)	119.9(4)	118.6(3)	119.3(7)	120.3(2)

Table 4 EPR spectroscopic data recorded for cations and anions generated from 1 to 11

	Frozen solution data ^{<i>a</i>,<i>b</i>}				Fluid solution d	lata ^{<i>a</i>,<i>c</i>}	
Complex	g _x	gy	gz	g _{ave}	g _{iso}	A_{iso} /× 10 ⁻⁴ cm ⁻¹	$a_{iso}/\!\times 10^{-4}~\text{cm}^{-1}$
1+	1.994 (15)	2.012 (10)	2.027 (8.5)	2.011	2.011 (2.5)	7.2	3.5
1^{+d}	_ ``	_ ``	_ ``		2.012 (1.5)	7.6	3.7
1^{-d}					1.931 (10.0)	36.1	_
2 ⁺	1.992 (15)	2.010(10)	2.026 (10)	2.009	2.006 (2.75)	7.6	3.1
3+	1.992 (12.5)	2.010 (9)	2.027 (9)	2.010	2.008 (2.4)	7.6	3.2
3^{-d}	_ ` ´	_	_		1.929 (9.5)	35.8	
4+	1.993 (11)	2.010 (9)	2.027 (8.5)	2.010	2.007 (2.2)	8.4	3.1
5 ^{+d}	_ ``	_ ()	_ ``		2.012 (2.1)	10.1	2.7
5 ^{-d}			_		1.929 (15.0)	36.4	
11+	1.991(13)	2.009 (11)	2.027 (10)	2.009	2.010 (2.65)	6.6	2.9
6+	1.967 (33)	1.990 (20)	2.022 (27)	1.993	1.994 (5.5)	21.1	
6 ^{+ d}	_	_	_		1.995 (4.8)	23.4	
7+	1.975 (17)	1.995 (6.5)	2.025 (17.7)	1.998	1.995 (5.5)	22.4	
8+	1.971 (26)	1.991 (11.2)	2.024 (25)	1.995	1.994 (6.0)	22.3	
9+	1.974 (27)	1.993 (11)	2.027 (23)	1.998	1.995 (6.0)	22.8	
10 ^{+ d}				_	1.999 (6.1)	25.2	
10 ^{-d}	_	_	_	_	2.004 ^e		_

^{*a*} Values in brackets are linewidths, in Gauss, used for the simulation of the experimental spectra; estimated errors are ± 0.001 and $\pm 0.1 \times 10^{-4}$ cm⁻¹, for g-values and hyperfine couplings, respectively; samples prepared by chemical oxidation with *ca*. one equivalent of [Cp₂Fe][BF₄] in CH₂Cl₂ unless stated otherwise. ^{*b*} As a frozen glass in CH₂Cl₂:dmf (4:1, v/v) at 77 K. ^{*c*} In CH₂Cl₂ at 210 K, unless stated otherwise. ^{*d*} Electrochemically generated in dmf containing [^{*n*}Bu₄N][BF₄] (0.2 M) at 273 K; frozen glass data at 77 K not recorded. ^{*e*} At 268 K, extensive hyperfine splittings were observed.

width required for simulation of these spectra (*e.g.* 15 G for $[5]^-$) is larger than that required for simulation of the EPR spectra of the corresponding cations (*e.g.* 2.1 G for $[5]^+$). Repeated attempts to generate $[1]^-$ by coulometry in order to permit EPR studies at 77 K failed to yield a spectrum that could be simulated satisfactorily.

Electrochemically generated [10]⁻ possesses an EPR spectrum that is consistent with the presence of an organic radical, possibly located on the quinoxalinyl moiety (Table 4; Fig. 8);^{35,36} this contrasts with the Mo analogue [5]⁻ that possesses an EPR spectrum which manifests coupling of the unpaired electron with ^{95,97}Mo (see Fig. S16†). The results of the DFT calculations (*vide infra*) provide an explanation of this significant difference between these closely related anions. Our attempts to simulate the experimental spectrum were unsuccessful.

DFT Calculations

We have undertaken DFT calculations for $[1]^z$ and $[6]^z$ (z = 0, +1 or -1), and 5 and 10 to provide a qualitative description of the structure and bonding within these compounds.

Selected bond lengths and interbond angles obtained from the DFT calculations for $[1]^z$ and $[6]^z$ (z = 0, +1 or -1) are presented in Table 5.

The theoretical studies reproduce magnitude of the bond lengths and the interbond angles within the {MSCCS} metallacycle of 1 and $[1]^+$ and the sense of the asymmetry observed by crystallography. Also, the magnitude of the decrease in the length of the C-S bonds and the increase in the length of the C-C bond that are observed by crystallography upon oxidation of 1 to $[1]^+$ is reproduced. However, in contrast to the slight decrease in the length of the Mo-S bonds observed upon oxidation, the DFT calculations predict a slight increase in the length of these bonds. This discrepancy parallels the corresponding observations for $[Cp_2M(dithiolene)]$ [M = Mo or W; dithiolene = dmit or dsit (= 2thioxo-1,3-dithiole-4,5-dithiolate)].17 Similar trends in the changes in the lengths of the M-S, C-S and C-C bonds are also observed in the calculated geometries of 6 and $[6]^+$ for which there are no experimentally determined X-ray crystallographic structures. The geometries calculated for $[1]^-$ and $[6]^-$ involve an elongation of the M-S bonds and small changes in the length of the C-S and C-C bonds relative to those for 1 and 6, respectively (Table 5). This is



Fig. 5 (a) X-band EPR spectra of $[Cp_2Mo(sdt)]^+$ ([1]⁺): lower trace, spectrum recorded for [1]⁺ (1 mM) in CH₂Cl₂:dmf (4:1 v/v) at 210 K, [1]⁺ was generated by the oxidation of 1 with *ca*. 1 equivalent of $[Cp_2Fe][BF_4]$; upper trace, simulation of the experimental spectrum using the parameters given in Table 4 and a Lorentzian line shape. (b) X-band EPR spectra of $[Cp_2Mo(S_2C_2(Me)(pyridin-2-yl))]$ ([11]⁺): lower trace, spectrum recorded for [11]⁺ (1 mM) in CH₂Cl₂:dmf (4:1 v/v) at 210 K, [11]⁺ was generated by the oxidation of 11 with *ca*. 1 equivalent of $[Cp_2Fe][BF_4]$; upper trace, simulation of the experimental spectrum using the parameters given in Table 4 and a 80% Gaussian and 20% Lorentzian line shape.



Fig. 6 X-band EPR spectra of $[Cp_2W(sdt)]^+$ ([6]⁺): lower trace, spectrum recorded for electrochemically generated [6]⁺ (1 mM) in dmf containing [^aBu₄N][BF₄] (0.2 M) at 273 K; upper trace, simulation of the experimental spectrum using the parameters given in Table 4 and a Lorentzian line shape.

consistent with a SOMO (Singly Occupied Molecular Orbital) in $[1]^-$ and $[6]^-$ that is π -antibonding with respect to the M–S bonds (*vide infra*). The values calculated for the metalladithiolene fold angle (θ) in 1 and $[1]^+$ reproduce the trend in the experimentally determined geometries in which the MoS₂ and S₂C₂ planes are essentially co-planar in 1 and are significantly folded in $[1]^+$.



Fig. 7 X-band EPR spectra of $[Cp_2Mo(sdt)]^-$ ([1]⁻): lower trace, spectrum recorded for electrochemically generated [1]⁻ (1 mM) in dmf containing ["Bu₄N][BF₄] (0.2 M) at 273 K; upper trace, simulation of the experimental spectrum using the parameters given in Table 4 and a Lorentzian line shape. * indicates a small quantity of [1]⁺ generated at the secondary electrode during the *in situ* generation of [1]⁻.



Fig. 8 X-band EPR spectra of electrochemically generated $[Cp_2W(qedt)]^{-1}$ ([10]⁻) in dmf containing ["Bu₄N][BF₄] (0.2 M) at 273 K.

The significant difference between the theoretical (14.45°) and experimental $(7.79(16)^{\circ})$ values of θ in [1]⁺ may be associated with a low energy barrier to folding about the S–S axis as has been established for other [Cp₂M(dithiolene)]⁺ (d^1) complexes.¹³⁻¹⁷

The composition of the frontier orbitals of **1** and **6** are summarised in Table 6 and 7, respectively, and illustrated for **1** in Fig. 9. The HOMO is primarily (65.0%) the dithiolene π_3 orbital that has C–C π -bonding and C–S antibonding character. Similar results have been obtained by DFT calculations for [Cp₂M(dmit)].¹⁷ The LUMO of **1** is composed of Mo d_{yz} (51.3%) and Cp₂ (27.9%) orbitals with a small (19.5%) contribution from

Table 5 Selected bond lengths and interbond angles obtained from the DFT calculations for $[1]^z$ and $[6]^z$ (z = 0, +1 or -1)^{*a*}

Complex	1	1+	1-	6	6+	6-
Bond lengths/Å						
M-S(1)	2.406 [2.4402(7)]	2.462 [2.4135(13)]	2.430	2.436	2.457	2.456
M-S(2)	2.404 [2.4396(7)]	2.466 [2.4252(14)]	2.425	2.428	2.461	2.440
S(1) - C(1)	1.747 [1.746(3)]	1.709 [1.666(5)]	1.749	1.759	1.709	1.746
S(2) - C(2)	1.782 [1.771(3)]	1.744 [1.714(5)]	1.800	1.794	1.747	1.799
C(1) - C(2)	1.357 [1.327(3)]	1.389 [1.370(7)]	1.362	1.353	1.391	1.365
Bond angles/°						
S(1) - M - S(2)	81.7 [82.29(2)]	81.3 [81.77(4)]	81.9	82.5	81.8	82.0
M - S(1) - C(1)	106.1 [106.07(8)]	106.7 [106.14(17)]	107.7	106.6	106.4	106.2
M - S(2) - C(2)	109.2 [106.85(8)]	106.9 [107.07(17)]	108.7	107.9	107.7	107.6
S(1)-C(1)-C(2)	123.0 [124.2(2)]	124.7 [125.3(4)]	123.8	124.1	124.9	124.4
S(2)-C(2)-C(1)	118.0 [120.5(2)]	119.0 [119.0(4)]	117.9	118.9	119.0	118.4
$\theta/^{\circ}$	0.02 [0.0]	14.45 [7.79(16)]	0.56	0.25	4.07	10.93

^a Data in square brackets are experimental values obtained from crystallographic studies of 1 and [1][BF₄].

Table 6 The nature, energy and composition of the frontier orbitals obtained from the DFT calculations for the geometry optimised structure of 1

Orbital			Energy/eV	% Contri			
Designation		Nature		Cp ₂	Мо	S_2C_2	Ph
105	LUMO+5	Ph	-0.81	2.4	0.9	1.1	95.6
104	LUMO+4	$S_2C_2 \pi_4 + Ph + Mo d_{xy}$	-1.21	4.4	6.3	31.6	57.7
103	LUMO+3	Mo $d_{x^2-y^2} + d_{z^2} + S_2C_2\sigma_1$	-1.43	28.6	56.2	14.5	0.8
102	LUMO+2	Mo d_{xz} + Cp ₂ + S ₂ C ₂ σ_2	-1.60	33.2	36.3	25.7	4.7
101	LUMO+1	$Mod_{xx} + Cp_2$	-2.04	39.8	50.1	6.7	3.2
100	LUMO	Mo $d_{yz} + S_2C_2 \pi_3 + Cp_2$	-2.73	27.9	51.3	19.5	1.0
99	HOMO	$S_2C_2 \pi_3 + Mo d_{yz}$	-3.99	20.2	6.7	65.0	8.1
98	HOMO-1	$Mo d_z^2$	-4.39	11.5	76.9	10.8	0.8
97	HOMO-2	$S_2C_2\pi_2 + Ph$	-5.31	11.2	1.9	59.6	27.3
96	HOMO-3	$S_2C_2\pi_2 + Ph$	-5.86	12.5	6.2	41.2	40.1
95	HOMO-4	$Ph + S_2C_2 \pi_2$	-5.92	10.0	2.2	23.8	64.0
94	HOMO-5	$S_2C_2 \sigma_2 + Mo d_{xz}$	-6.01	16.3	4.2	43.0	36.5
93	HOMO-6	$S_2C_2\sigma_1 + Mod_{r^2}$	-6.53	13.2	12.9	70.2	3.7
92	HOMO-7	$Cp_2 + Mo d_{yz}$	-6.75	42.3	19.3	17.2	21.2
91	HOMO-8	$Cp_2 + Mo d_{xz}$	-6.96	65.6	23.8	10.2	0.3
90	HOMO-9	$\hat{Cp}_2 + Mo d_{xz}$	-7.45	58.4	29.4	11.6	0.6

the dithiolene π_3 -orbital. LUMO+1, LUMO+2, and LUMO+3 each have a similar composition to the LUMO and involve the Mo d_{xy} , Mo d_{xz} and Mo d_{x2y2} orbitals, respectively. LUMO+4 is mainly (57.7%), and LUMO+5 virtually exclusively (95.6%), phenyl π^* in character. The bonding in **6** is very similar to that in **1**; the major differences being that the LUMO is higher in energy in **6** (-1.70 eV, Table 6) relative to **1** (-2.73 eV, Table 7).

The results of the DFT calculations performed for the $[1]^{2}$ and $[6]^{z}$ (z = +1, 0, or -1) complexes provide insight into the nature of the EPR spectra of $[1]^z$ and $[6]^z$ (z = +1 or -1) and the corresponding ions of related species. Fig. 10 illustrates the nature, and indicates the energy, of the HOMOs of 1 and 6 and the SOMOs of [1]⁺, [6]⁺, [1]⁻ and [6]⁻. The SOMO of [1]⁺ and [6]⁺ is primarily dithiolene π_3 -based (66.6% and 70.8%, respectively) with a minor contribution from the metal d_{x^2,y^2} and d_{z^2} orbitals (12.6% and 3.6%, respectively). Given the nature of the HOMO of **1** and **6** (Table 6) and the SOMO of $[1]^+$ and $[6]^+$ (Fig. 10), OX¹ for all of the compounds investigated herein is considered to be primarily a dithiolene-based process. This is consistent with the potential of OX^1 of both the Mo (1 to 5) and W (6 to 10) groups of compounds varying with the nature of the dithiolene substituent (Table 1). Also, the similarity in the energies of 1 and 6 and [1]⁺ and [6]⁺ (Fig. 10) explains the similarity in the value

of redox potentials for OX^1 for 1 and 6 and the other pairs of related compounds (Table 1), *i.e.* OX^1 for a W compound is *ca*. 30 mV less than its Mo counterpart. Furthermore, the sense of this difference in redox potentials is consistent with the results of the DFT calculations.

In respect of the EPR spectra recorded for $[1]^+$ (Fig. 5(a), S12 and S13[†]) the observation of a relatively small hyperfine coupling to ^{95,97}Mo (I = 5/2) and the presence of coupling to a unique proton (I = 1/2) is consistent with the nature of the SOMO of this cation [Fig. 10(c)], with the unique proton being the dithiolene hydrogen. These considerations are applicable to $[2]^+$, $[3]^+$, $[4]^+$ and $[5]^+$, since their EPR spectra closely resemble that of $[1]^+$, and to $[11]^+$, the EPR spectrum of which [Fig. 5(b)] manifests coupling of the unpaired electron both to ^{95,97}Mo and three protons (*i.e.* the CH₃ substituent of the dithiolene). Similar observations are made in respect of the EPR spectra recorded for the W complexes $[6]^+$ to $[10]^+$, although coupling of the unpaired electron to the dithiolene proton was not observed in the experimental spectra (*e.g.* Fig. 6 and S14[†]), possibly due to the greater linewidths of these spectra.

The DFT calculations accomplished for 1 and 6 indicate that the LUMO is significantly higher in energy in 6 than in 1 (Tables 6 and 7). This is consistent with the value of RED¹ for a W compound

Orbital			Energy/eV	% Contri			
Designation		Nature		Cp_2	W	S_2C_2	Ph
121	LUMO+5	Ph	-0.70	2.1	0.7	1.4	95.9
120	LUMO+4	$S_2C_2 \pi_4 + Ph + W d_{xy}$	-0.96	21.8	28.7	13.6	21.8
119	LUMO+3	$W d_{x^2-v^2} + d_{z^2} + S_2 C_2 \sigma_1$	-1.24	33.0	37.0	20.7	33.0
118	LUMO+2	$W d_{xy} + Cp_2$	-1.40	27.6	37.5	17.0	17.9
117	LUMO+1	$W d_{xz} + Cp_2 + S_2C_2 \sigma_2$	-1.57	40.8	36.2	19.8	3.2
116	LUMO	$W d_{yz} + S_2 C_2 \pi_3 + C p_2$	-1.70	36.7	51.5	11.3	0.5
115	HOMO	$S_2C_2\pi_3 + Wd_{yz}$	-3.75	12.9	2.9	76.0	8.3
114	HOMO-1	$W d_{x^2-v^2} + d_{z^2}$	-4.42	19.8	69.0	10.3	1.0
113	HOMO-2	$S_2C_2\pi_2 + Ph$	-5.12	10.7	1.9	63.7	23.7
112	HOMO-3	$S_2C_2 \pi_2 + Ph$	-5.79	3.2	2.2	14.6	80.1
111	HOMO-4	$Ph + S_2C_2 \pi_2$	-5.79	9.5	2.3	32.9	55.3
110	HOMO-5	$S_2C_2 \sigma_2 + W d_{xz}$	-5.98	16.3	7.7	63.1	12.9
109	HOMO-6	$S_2C_2 \sigma_1 + W d_{z^2}$	-6.51	12.8	14.8	68.4	4.0
108	HOMO-7	$Cp_2 + W d_{vz}$	-6.83	40.8	14.4	24.1	20.7
107	HOMO-8	$\hat{Cp}_2 + W d_{xz}$	-7.00	68.8	22.3	8.0	0.6
106	HOMO-9	$\bar{Cp}_2 + W d_{x^2-y^2} + d_{z^2}$	-7.51	67.4	24.9	4.8	2.9

Table 7 The nature, energy and composition of the frontier orbitals obtained from the DFT calculations for the geometry optimised structure of 6

Table 8 Crystallographic data for 1, [1][BF₄], 3, [3][BF₄], [8][BF₄] and 9

Complex	1	[1][BF ₄]	3	[3][BF ₄]	[8][BF ₄]	9
Formula	$C_{18}H_{16}S_2Mo$	$C_{18}H_{16}S_2MoBF_4$	C ₁₇ H ₁₅ NS ₂ Mo	C ₁₇ H ₁₆ NS ₂ MoBF ₄	$C_{17}H_{15}NS_2WBF_4$	$C_{17}H_{15}NS_2W$
M	392.37	479.18	393.37	481.18	568.08	481.27
Colour	Red	Dark red	Purple	Dark red	Brown	Deep red
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinc
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/a$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	8.8648(8)	6.7275(5)	10.732(2)	6.9390(10)	6.9700(9)	10.5703(14)
b/Å	15.5930(10)	14.5860(10)	16.083(2)	14.514(2)	14.514(2)	11.879(2)
c/Å	10.8010	18.3070(10)	8.660(2)	17.696(3)	17.689(2)	11.992(2)
β (°)	90.990(2)	98.2730(10)	90.16(2)	101.018(3)	100.907(10)	97.136(2)
$U/Å^3$	1492.8(2)	1777.7(2)	1494.6(4)	1749.4(5)	1757.1(4)	1494.1(4)
Ζ	4	4	4	4	4	4
T/K	150	150	296	150	203(2)	150
$D_{\rm c}/{\rm g~cm^{-3}}$	1.746	1.790	1.748	1.827	2.147	2.140
<i>F</i> (000)	792	956	792.00	960	1084	920
μ/cm^{-1}	11.5 (Mo-Kα)	10.11 (Mo-Kα)	98.15 (Cu-Kα)	10.3 (Mo-Kα)	68.53 (Mo-Kα)	80.02 (Mo-Kα)
Diffractometer	Bruker SMART	Bruker SMART	Rigaku AFC5R	Bruker SMART	Enraf-Nonius	Bruker SMART
	CCD area detector	CCD area detector		CCD area detector	CAD-4	CCD area detector
Crystal dimensions/mm	$0.27 \times 0.18 \times 0.05$	$0.20 \times 0.20 \times 0.12$	$0.10\times0.12\times0.35$	$0.54 \times 0.14 \times 0.10$	$0.25 \times 0.15 \times 0.1$	$0.3 \times 0.1 \times 0.1$
λ/Å	0.71073	0.71073	1.54178	0.71073	0.71073	0.71073
$2\theta_{\rm max}$ (°)	57.5	57.48	156.0	57.5	49.94	57.2
Scan type	ω	ω	ω-2θ	ω	Ψ	ω
Total data	9524	15612	3276	11124	3343	15505
Unique data	3471	4176	3107	4270	3082	3608
'Observed' data, $N_o [I > 2\sigma(I)]$	2774	3265	2284	2717	2147	3275
Least square variables, N_v	190	217	191	246	234	190
R	0.028	0.048	0.046	0.046	0.040	0.019
R_w	0.062	0.129	0.045	0.112	0.070	0.48
S	0.96	1.064	2.47	0.967	1.027	1.019
Difference map features/e Å ⁻³	0.65, -0.54	1.040, -0.939	0.78, -1.22	0.86, -1.02	0.918, -0.671	0.948, -0.907

(6 to 9) being significantly (*ca.* 300 mV) more negative (Table 1) than that of its Mo counterpart (1 to 4).

The SOMOs of both [1]⁻ [Fig. 10(e)] and [6]⁻ [Fig. 10(f)] possess significant metal character involving the Mo d_{yz} and W $d_{x^2-y^2}$ and d_{yz} orbitals (the total Mo and W contributions are 47.1% and 53.6%, respectively), together with contributions from the two Cp groups (18.7% and 24.9%, respectively) and the dithiolene π_3 orbital (30.3% and 17.6%, respectively). Thus, the unpaired electron is more localised on the metal in mono-anions than in the mono-cations. In agreement with these results, the EPR spectrum of each of the molybdenum containing mono-anions ([1]⁻, Fig. 7,

to $[5]^-$) manifests a larger ^{95,97}Mo coupling (A_{iso}) than is observed for the corresponding mono-cation. Also, in contrast to the EPR spectra of $[1]^+$ (Fig. 5(a)) to $[5]^+$, the EPR spectra of $[1]^-$ (Fig. 7) to $[5]^-$ do not manifest coupling to the dithiolene hydrogen.

For **10**, two aspects of the reduction are surprising. First, the value of RED¹ is significantly less negative than expected from the values of RED¹ for **5** and compounds **6** to **9** (Table 1). Second, the EPR spectrum of $[5]^-$ is consistent with the information presented above, *i.e.* the unpaired electron is located in an orbital with a significant Mo contribution, by contrast the EPR spectrum $[10]^-$ (Fig. 8) is typical of an organic radical. The energies and the



Fig. 9 Energy level diagram and pictorial representations of the Kohn–Sham frontier orbitals of $[Cp_2Mo(sdt)]$ (1).



Fig. 10 Pictorial representations and energies of the Kohn–Sham HOMOs of: (a) $[Cp_2Mo(sdt)]$ (1) and (b) $[Cp_2W(sdt)]$ (6) and the SOMOs of: (c) [1]⁺; (d) [6]⁺; (e) [1]⁻ and (f) [6]⁻.

nature of the frontier MOs of **5** and **10** obtained from the DFT calculations are illustrated in Fig. 11. Thus, the LUMO in **10** is at a significantly lower energy than that in **5** and is a quinoxalinyl-based π -orbital, whereas in **5** the LUMO involves a significant metal contribution (*cf.* **1**, Table 6) and the quinoxalinyl-based orbital is the LUMO+1. These results explain why the potential



Fig. 11 Pictorial representations and energies of the Kohn–Sham frontier orbitals of: (a) $[Cp_2Mo(qedt)]$ (5) and (b) $[Cp_2W(qedt)]$ (10).

of RED¹ for **10** is less negative by *ca*. 230 mV than expected and the EPR spectrum of $[10]^-$ is characteristic of an organic radical, *i.e.* {quinoxaliny}⁻⁻.

Experimental

General

Quinoxaline, 2-, 3- and 4-acetylpyridine and bromoacetophenone were obtained from Lancaster Synthesis Ltd. $[Cp_2MCl_2]$ (M = Mo or W) were obtained from Strem Chemicals. Anhydrous methanol and *N*,*N*-dimethylformamide (dmf) were purchased from Aldrich and Fluka, respectively. All other solvents were dried by standard techniques. Column chromatography was performed on alumina (Brockmann Grade II). The pro-ligands R-1,3-dithiol-2-one (R = phenyl, pyridin-2-yl, pyridin-3-yl, pyridin-4-yl or quinoxalin-2-yl)^{9,37,38} and $[Cp_2Fe][BF_4]^{39}$ were synthesised by published procedures. The pro-ligand 4-(pyridin-2-yl)-5-(methyl)-1,3-dithiol-2-one was synthesised by the method of Dinsmore *et al.*⁹ All reactions were performed under an atmosphere of argon using standard Schlenk-line techniques.

Microanalyses were conducted by the staff of the Microanalytical Service of the Department of Chemistry, The University of Manchester and of the School of Chemistry, The University of Nottingham. For 2 and 10, the C analyses differ from those expected; however, spectroscopic data support the proposed formulation.

CI mass spectra were recorded on a Fisons VG Trio 200 or a Fisons VG Autospec mass spectrometer. ¹H NMR spectra were recorded on a Varian Inova 300 or a Bruker DPX300 spectrometer and 125 Hz ¹³C NMR spectra were recorded on a Varian Inova 500 spectrometer. The air-sensitive nature of the [Cp₂M(dithiolene)] (M = Mo or W) compounds resulted in a broadening of ¹H resonances of the dithiolene group due to the formation of a small amount of paramagnetic [Cp₂M(dithiolene)]⁺; the addition of a small quantity of [Cp₂Co] (as specified in the Synthesis section) gave complete resolution of all proton environments without affecting their chemical shifts.

Cyclic voltammetric and coulometric studies were carried out using an Autolab PGSTAT20 potentiostat. Standard cyclic voltammetric measurements were accomplished for the solution of interest under an atmosphere of argon using a three-electrode arrangement in a single compartment cell. The cell comprised a glassy carbon working electrode, a Pt wire secondary electrode and a saturated calomel reference electrode, chemically isolated from the test solution *via* a bridge tube containing electrolyte solution and fitted with a porous vycor frit. The compound of interest was present at a concentration of 10^{-3} M in dmf and the solution contained ["Bu₄N][BF₄] (0.2 M) as the supporting electrolyte. Cyclic voltammograms were recorded at ambient temperature in the scan rate range 20–300 mV s⁻¹. Redox potentials are quoted *versus* the [Cp₂Fe]⁺/[Cp₂Fe] couple used as an internal reference. Compensation for internal resistance was not applied.

The redox changes of each of the compounds 1 to 10 at 273 K in dmf solution containing $[^{n}Bu_{4}N][BF_{4}]$ (0.2 M) as the supporting electrolyte were monitored by UV/vis spectroelectrochemical studies using an optically transparent electrode (OTE).⁴⁰ Spectra were recorded between 270 and 900 nm using a Perkin Elmer Lambda 16 spectrophotometer in conjunction with a Sycopel Scientific Ltd. DD10M potentiostat and a saturated calomel reference electrode. Changes in the UV/vis/NIR spectra between 270 and 1800 nm for the one-electron oxidations of 1, 3, 5, 6, 8 and 10 as ca. 10^{-3} M solutions containing ["Bu₄N][BF₄] (0.2 M) as the supporting electrolyte at 273 K were monitored using a PerkinElmer 9 spectrophotometer in conjunction with a Metrohm Polarecord E506 potentiostat and a Ag/Ag⁺ reference electrode. For the latter spectroelectrochemical studies the cell was a modified quartz cuvette of optical path length 0.5 mm and involved three-electrodes: a Pt/Rh gauze working electrode; a Pt wire secondary electrode (held in a fritted PTFE sleeve); and a reference electrode chemically isolated from the test solution via a bridge tube containing the electrolyte solution and terminating in a porous frit. The cavity was purged with dinitrogen and temperature of the sample was controlled by flowing cooled dinitrogen across the surface of the cell.

Each spectroelectrochemical study involved a single potential step. The operating potential applied to the working electrode was typically >100 mV more positive than $E_p{}^a$ for an oxidation experiment and >100 mV more negative than $E_p{}^c$ for a reduction. A redox process was considered complete when consecutive spectra were identical. The chemical reversibility of a process was investigated by application of a potential at the working electrode that was sufficient to re-reduce an electrogenerated oxidation product or to re-oxidise an electrogenerated reduction product. The applied potential was typically >100 mV more negative than $E_p{}^c$ to reverse an oxidation process and >100 mV more positive than $E_p{}^a$ to reverse a reduction process. The process was considered to be electrochemically reversible if the spectroscopic profile of the starting material was reproduced.

In situ electrochemical EPR studies were performed with a standard quartz tube of internal diameter 3 mm into which was inserted a modified version of the 3-electrode arrangement described by Hartl *et al.*⁴¹ The working, secondary and pseudo-reference electrodes were a Pt helix, a Pt wire and a Ag wire, respectively. X-band EPR spectra were recorded on either a Bruker ESP300E or Bruker EMX spectrometer and simulated using WINEPR SimFonia, Shareware version 1.25, Brüker Analytische Messtechnik GmbH.

Syntheses

 $[Cp_2Mo(sdt)]$ (sdt = $-SC(H)C(C_6H_5)S^-$) (1). CsOH·H₂O (227 mg, 1.35 mmol) was dissolved in anhydrous MeOH (5 cm³). 4-(Phenyl)-1,3-dithiol-2-one (125 mg, 0.64 mmol) was added and the mixture stirred for 15 min producing a yellow/brown solution. [Cp₂MoCl₂] (195 mg, 0.65 mmol) and MeOH (5 cm³) were then added and the mixture stirred overnight at room temperature. The solvent was removed under a reduced pressure to yield a black solid. Column chromatography of the reaction mixture on alumina gave, on elution with CH₂Cl₂, the product as a single deep purple band which was collected and evaporated to dryness. The black solid was dissolved in a minimum volume of CH₂Cl₂ and nhexane was added until the product precipitated as a black/purple solid. The solvent was removed by decantation and the product dried under reduced pressure. Yield 169 mg, 67%. Anal. Calcd. for C₁₈H₁₆MoS₂: C, 55.09; H, 4.10%. Found: C, 54.80; H, 4.16%. ¹H NMR (300 MHz, CDCl₃ + Cp₂Co): δ 7.70 (d, [J_{H-H} = 8.2 Hz], 2 H, H², H⁶), 7.27 (m, 2H, H³, H⁵), 7.13 (t, $[J_{H-H} = 7.4 \text{ Hz}]$, 1 H, H⁴), 6.82 (s, 1 H, H^{dithiolene}), 5.31 (s, 10 H, $2C_5H_5$). ¹³C NMR (125 MHz, CDCl₃ + Cp₂Co): δ 140.3 (C^{1'/1}), 140.1 (C^{1'/1}), 127.7 (C³, C⁵), 125.9 (C², C⁶), 125.4 (C^{dithiolene}), 124.2 (C⁴), 98.2 (C₅H₅). Mass Spectrum (CI): *m/z* 395 [Cp₂Mo(sdt)+H]⁺. IR (KBr disc): 3114 (w), 3078 (w), 3066 (w), 1637 (m), 1589 (m), 1534 (s), 1483 (m), 1437 (m), 1085 (m), 1074 (m), 1016 (s), 1002 (m), 900 (w), 808 (vs) 749 (vs), 696 (m), 546 (m) cm⁻¹.

1 was dissolved in CH_2Cl_2 and the diffusion of *n*-hexane into a CH_2Cl_2 solution of **1** gave red rectangular crystals. $[Cp_2Mo(sdt)][BF_4]$, $([1^*][BF_4])$ was prepared by stirring **1** (9 mg, 2.29×10^{-5} mol) and $[Cp_2Fe][BF_4]$ (6 mg, 2.19×10^{-5} mol) in CH_2Cl_2 (2 cm³) for 2 h. The resultant green solution was filtered then layered with toluene and the mixture yielded red crystals upon standing at room temperature.

 $[Cp_2Mo(2-pedt)]$ (2-pedt = $-SC(H)C((C_5H_4N)-2)S^-)$ (2). 2 was prepared as described for 1, from CsOH·H₂O (229 mg, 1.36 mmol), 4-(pyridin-2-yl)-1,3-dithiol-2-one (130 mg, 0.66 mmol) and [Cp₂MoCl₂] (197 mg, 0.66 mmol), and obtained as a black solid. Column chromatography of the reaction mixture on alumina gave, on elution with CH2Cl2:MeOH (99:1), the product as a single deep purple band which was collected and evaporated to dryness. The black solid was dissolved in a minimum volume of CH2Cl2 and n-hexane was added until the product precipitated as a black/purple solid. The solvent was removed by decantation and the product dried under reduced pressure. Yield 131 mg, 50%. Anal. Calcd. for C₁₇H₁₅NMoS₂: C, 51.90; H, 3.84; N, 3.56%. Found: C, 48.80; H, 3.52; N, 3.26%. ¹H NMR (300 MHz, CDCl₃ + Cp₂Co): δ 8.42 (d, [J_{H-H} = 4.4 Hz], 1 H, H⁶), 7.61 (d, $[J_{H-H} = 8.1 \text{ Hz}]$, 1 H, H³), 7.43 (m, 1 H, H⁴), 7.34 (s, 1 H, H^{dithiolene}), 6.87 (m, 1 H, H⁵), 5.23 (s, 10 H, 2C₅H₅). ¹³C NMR (125 MHz, CDCl₃): δ 157.3 (C^{1'/2}), 148.4 (C⁶), 140.5 (C11/2), 135.5 (C4), 130.9 (Cdithiolene), 119.7 (C3/5), 119.5 (C3/5), 98.1 (C_5H_5) . Mass Spectrum (CI): m/z 396 $[Cp_2Mo(2-pedt)+H]^+$. IR (KBr disc): 3098 (w), 3062 (w), 1577 (s), 1562 (m), 1517 (vs), 1460 (vs), 1438 (w), 1420 (m), 1377 (w), 1364 (w), 1268 (w), 1016 (w), 1000 (w), 920 (m), 831 (s), 815 (vs), 767 (s), 730 (m), 701 (w), 671 (m), 635 (w), 607 (w), 587 (w), 599 (w) cm⁻¹.

 $[Cp_2Mo(3-pedt)]$ (3-pedt = $-SC(H)C((C_5H_4N)-3)S^-)$ (3). 3 was prepared as described for 1, from CsOH·H₂O (255 mg, 1.50 mmol),

4-(pyridin-3-yl)-1,3-dithiol-2-one (142 mg, 0.72 mmol) and $[Cp_2MoCl_2]$ (201 mg, 0.67 mmol) and purified as described for **2** to give a black/purple solid. Yield 155 mg, 58%. Anal. Calcd. for $C_{17}H_{15}NMoS_2$: C, 51.90; H, 3.84; N, 3.56%. Found: C, 51.67; H, 3.83; N, 3.54%. ¹H NMR (300 MHz, CDCl_3): δ 8.80 (d, $[J_{H-H} = 1.7 \text{ Hz}]$, 1 H, H²), 8.23 (dd, $[J_{H-H} = 1.3, 4.6 \text{ Hz}]$, 1 H, H⁶), 7.84 (m, 1 H, H⁴), 6.87 (m, 1 H, H⁵), 6.84 (s, 1 H, H^{dithiolene}), 5.22 (s, 10 H, 2C₅H₅). ¹³C NMR (125 MHz, CDCl_3): δ 147.1 (C²), 146.0 (C⁶), 136.8 (C^{17/3}), 132.7 (C⁴), 126.5 (C^{dithiolene}), 122.6 (C⁵), 98.2 (C₅H₅). Mass Spectrum (CI): *m/z* 396 [Cp₂Mo(3-pedt)+H]⁺. IR (KBr disc): 1560 (m), 1532 (vs), 1508 (m), 1474 (m), 1438 (m), 1402 (m), 1098 (m), 1087 (m), 1066 (m), 1039 (m), 1021 (s), 1005 (m), 908 (w), 828 (s), 816 (vs), 801 (m), 766 (s), 668 (w), 550 (w) cm⁻¹.

Purple needle-shaped crystals of **3** were grown by the slow diffusion of *n*-hexane into a solution of **3** in CDCl₃. [Cp₂Mo(3-pedt)][BF₄] ([**3**⁺][BF₄]) was prepared by stirring **3** (9 mg, 2.29 × 10^{-5} mol) and [Cp₂Fe][BF₄] (5 mg, 1.83×10^{-5} mol) in CH₂Cl₂ for 2 h. The resultant green solution was filtered then layered with toluene and the mixture yielded red crystals upon standing at room temperature.

[Cp₂Mo(4-pedt)] (4-pedt = ${}^{-}SC(H)C((C_5H_4N)-4)S^-$) (4). 4 was prepared as described for 1, from CsOH·H₂O (230 mg, 1.36 mmol), 4-(pyridin-4-yl)-1,3-dithiol-2-one (132 mg, 0.67 mmol) and [Cp₂MoCl₂] (120 mg, 0.40 mmol) and purified as described for 2 to give a black/purple solid. Yield 113 mg, 71%. Anal. Calcd. for C₁₇H₁₅NMoS₂: C, 51.90; H, 3.84; N, 3.56%. Found: C, 50.76; H, 3.86; N, 3.25%. ¹H NMR (300 MHz, CDCl₃): δ 8.32 (d, [*J*_{H-H} = 4.8 Hz], 2 H, H², H⁶), 7.45 (d, [*J*_{H-H} = 4.8 Hz], 2 H, H³, H⁵), 7.07 (s, 1 H, H^{dithiolene}), 5.22 (s, 10 H, 2C₅H₅). ¹³C NMR (125 MHz, CDCl₃): δ 148.9 (C², C⁶), 130.7 (C^{dithiolene}), 120.1 (C³, C⁵), 98.2 (C₅H₅). Mass Spectrum (CI): *m/z* 396 [Cp₂Mo(4-pedt)+H]⁺.IR (KBR disc): 2954 (m), 1599 (m), 1585 (vs), 1541 (m), 1513 (s), 1260 (m), 1209 (w), 1015 (m), 988 (m), 918 (m), 832 (vs), 812 (m), 771 (s), 730 (m), 702 (w), 673 (w), 652 (m), 607 (m), 556 (w) cm⁻¹.

[Cp₂Mo(qedt)] (qedt = ${}^{-}SC(H)C(C_6H_4N_2C_2H)S^-$) (5). 5 was prepared and purified as described for 1, from CsOH·H₂O (83 mg, 0.49 mmol), 4-(quinoxalin-2-yl)-1,3-dithiol-2-one (61 mg, 0.25 mmol) and [Cp₂MoCl₂] (83 mg, 0.28 mmol), and was obtained as a purple solid. Yield 48 mg, 44%. Anal. Calcd. for C₂₀H₁₆N₂MoS₂: C, 54.05; H, 3.63; N, 6.30%. Found: C, 53.15; H, 3.53; N, 6.86%. ¹H NMR (300 MHz, CDCl₃): δ 9.27 (s, 1 H, H³), 8.09 (d, [J_{H-H} = 8.2 Hz], 1 H, H^{5/8}), 7.96 (d, [J_{H-H} = 8.1 Hz], 1 H, H^{5/8}), 7.82 (s, 1 H, H^{dithiolene}), 7.63 (m, 1 H, H^{6/7}), 7.56 (m, 1 H, H^{6/7}), 5.35 (s, 10 H, 2C₃H₅). Mass Spectrum (CI): *m/z* 446 [Cp₂Mo(qedt)+H]⁺.

[Cp₂W(sdt)] (6). CsOH·H₂O (185 mg, 1.10 mmol) was dissolved in anhydrous MeOH (5 cm³). 4-(Phenyl)-1,3-dithiol-2-one (115 mg, 0.59 mmol) was added and the mixture stirred for 15 min producing a yellow/brown solution. [Cp₂WCl₂] (225 mg, 0.58 mmol) and CH₂Cl₂ (15 cm³) were then added and the mixture stirred overnight at room temperature. The solvent was removed under a reduced pressure to yield a brown solid. The solid was dissolved in CH₂Cl₂ and the solution filtered through alumina; the alumina was washed with CH₂Cl₂:MeOH (98:2) (3 × 5 cm³) to remove any absorbed product, the washings and the filtrate combined and the solvent removed under a reduced pressure to give a red solid. Column chromatography on alumina gave,

on elution with CH₂Cl₂, the product as a single orange band which was collected and evaporated to dryness. The red solid was dissolved in a minimum volume of CH₂Cl₂ and n-hexane added until the product precipitated as a red solid. The solvent was removed by decantation and the product dried under reduced pressure. Yield 56 mg, 20%. Anal. Calcd. for C₁₈H₁₆WS₂: C, 45.01; H, 3.36%. Found: C, 45.23; H, 3.12%. ¹H NMR (300 MHz, CDCl₃ + Cp₂Co): δ 7.60 (d, [J_{H-H} = 8.3 Hz], 2 H, H², H⁶), 7.15 (m, 2 H, H³, H⁵), 7.01 (t, $[J_{H-H} = 6.8 \text{ Hz}]$, 1 H, H⁴), 6.31 (s, 1 H, H^{dithiolene}), 5.18 (s, 10 H, 2C₅H₅). ¹³C NMR (125 MHz, CDCl₃ + Cp_2Co): δ 143.8 ($C^{1'/1}$), 139.0 ($C^{1'/1}$), 127.8 (C^3 , C^5), 126.5 (C^2 , C^6), 126.3 (Cdithiolene), 125.4 (C4), 94.8 (C5H5). Mass Spectrum (CI); m/z 481 [Cp₂W(sdt)+H]⁺. IR (KBr disc): 3118 (m), 3084 (m), 1589 (s), 1570 (m), 1536 (vs), 1483 (s), 1432 (m), 1384 (s), 1068 (m), 1012 (s), 999 (s), 916 (w), 899 (m), 832 (vs), 808 (vs), 779 (m), 749 (vs), 696 (s), 653 (m), 588 (w) cm⁻¹.

[Cp₂W(2-pedt)] (7). 7 was prepared and purified as described for 6, from CsOH·H₂O (203 mg, 1.23 mmol), 4-(pyridin-2-yl)-1,3-dithiol-2-one (121 mg, 0.61 mmol) and [Cp₂WCl₂] (236 mg, 0.61 mmol) and obtained as a red/brown solid. Yield 52 mg, 17%. Anal. Calcd for C₁₇H₁₅WNS₂: C, 42.42; H, 3.14; N, 2.91%. Found: C, 42.07; H, 3.31; N, 2.82%. ¹H NMR (300 MHz, CDCl₃ + Cp₂Co): δ 8.42 (d, [*J*_{H-H} = 4.3 Hz], 1 H, H⁶), 7.63 (d, [*J*_{H-H} = 7.9 Hz], 1 H, H³), 7.42 (m, 1 H, H⁴), 6.97 (s, 1 H, H^{dithiolene}), 6.85 (m, 1 H, H³), 5.17 (s, 10 H, 2C₅H₅).¹³C NMR (125 MHz, CDCl₃): δ 156.2 (C^{17/2}), 148.6 (C⁶), 144.4 (C^{17/2}), 135.6 (C⁴), 133.1 (C^{dithiolene}), 120.3 (C^{3/5}), 119.5 (^{C3/5}), 94.6 (C₅H₅). Mass spectrum (CI); *m/z* 482 [Cp₂W(2-pedt)+H]⁺. IR (KBr): 3105 (w), 3094 (w), 3083 (w), 1576 (s), 1519 (vs), 1459 (s), 1421 (s), 1147 (w), 1113 (w), 1087 (m), 1050 (m), 1014 (m), 997 (m), 922 (m), 834 (s), 814 (s), 767 (s), 669 (s) cm⁻¹.

[Cp₂W(3-pedt)] (8). 8 was prepared and purified as described for 6, from CsOH·H₂O (208 mg, 1.23 mmol), 4-(pyridin-3-yl)-1,3-dithiol-2-one (121 mg, 0.61 mmol) and [Cp₂WCl₂] (238 mg, 0.61 mmol), and obtained as an orange solid. Yield 75 mg, 25%. Anal. Calcd for C₁₇H₁₅NWS₂: C, 42.42; H, 3.14; N, 2.91. Found: C, 42.08; H, 3.28; N, 2.92. ¹H NMR (300 MHz, CDCl₃): δ 8.80 (d, [*J*_{H-H} = 2.3 Hz], 1 H, H²), 8.20 (dd, [*J*_{H-H} = 1.5, 4.6 Hz], 1 H, H⁶), 7.85 (m, 1 H, H⁴), 7.06 (m, 1 H, H⁵), 6.38 (s, 1 H, H^{dithiolene}), 5.16 (s, 10 H, 2C₅H₅). ¹³C NMR (125 MHz, CDCl₃): δ 147.8 (C²), 146.1 (C⁶), 140.8 (C^{17/3}), 134.9 (C^{17/3}), 133.2 (C⁴), 128.8 (C^{dithiolene}), 122.6 (C⁵), 94.8 (C₅H₅). Mass spectrum (CI): *m/z* 482 [Cp₂W(3pedt)+H]⁺. IR (KBr): 3109 (m), 3082 (m), 1577 (w), 1560 (m), 1531 (s), 1473 (m), 1433 (m), 1403 (m), 1125 (w), 1019 (m), 1001 (m), 833 (s), 815 (s), 799 (m), 768 (s), 708 (m), 552 (w) cm⁻¹.

 $[Cp_2W(3-pedt)][BF_4]$ ([8⁺][BF₄]) was prepared by stirring 8 (6 mg, 1.25×10^{-5} mol) and $[Cp_2Fe][BF_4]$ (4 mg, 1.47×10^{-5} mol) in CH₂Cl₂ for 2 h. The resultant green solution was filtered then layered with toluene and the mixture yielded red crystals upon standing at room temperature.

[Cp₂W(4-pedt)] (9). 9 was prepared and purified as described for 6, from CsOH·H₂O (218 mg, 1.30 mmol), 4-(pyridin-4-yl)-1,3-dithiol-2-one (126 mg, 0.65 mmol) and [Cp₂WCl₂] (251 mg, 0.65 mmol) and obtained as an orange solid. Yield 111 mg, 35%. Anal. Calcd for C₁₇H₁₅NWS₂: C, 42.42; H, 3.14; N, 2.91%. Found: C, 41.88; H, 3.14; N, 2.90%. ¹H NMR (300 MHz, CDCl₃ + Cp₂Co): δ 8.31 (m, 2 H, H², H⁶), 7.46 (m, 2 H, H³, H⁵), 6.67 (s, 1 H, H^{dithiolene}), 5.19 (s, 10 H, $2C_5H_5$). ¹³C NMR (75 MHz, CDCl₃): δ 148.7 (C², C⁶), 141.7 (C¹⁷⁴), 133.6 (C^{dithiolene}), 120.8 (C³, C⁵), 94.7 (C₅H₅). Mass spectrum (CI): *m/z* 482 [Cp₂W(4-pedt)+H]⁺. IR (KBr): 3091 (w), 3079 (w), 3065 (w), 3057 (w), 1587 (vs), 1543 (s), 1516 (s), 1408 (w), 1210 (w), 1013 (w), 989 (m), 917 (w), 838 (s), 814 (m), 803 (m), 773 (m), 732 (w), 651 (w), 609 (w), 558 (w) cm⁻¹.

Deep red crystals of **9** were grown by the slow diffusion of n-hexane into a solution of **9** in CH_2Cl_2 .

[Cp₂W(qedt)] (10). 10 was prepared as described for 6, from CsOH·H₂O (132 mg, 0.79 mmol), 4-(quinoxalin-2-yl)-1,3-dithiol-2-one (96 mg, 0.39 mmol) and [Cp₂WCl₂] (139 mg, 0.36 mmol) and obtained as a red/brown solid. Column chromatography on alumina gave, on elution with CH₂Cl₂, the product as a single orange band which was collected and evaporated to dryness. The deep red solid was dissolved in a minimum volume of CH₂Cl₂ and *n*-hexane added until the product precipitated as a deep red solid. The solvent was removed by decantation and the product dried under a reduced pressure. Yield 28 mg, 15%. Anal. Calcd for C₂₀H₁₆N₂WS₂: C, 45.12; H, 3.03; N, 5.26%. Found: C, 43.32; H, 3.04; N, 4.94%. ¹H NMR (300 MHz, CDCl₃): δ 9.29 (s, 1 H, H²), 8.10 (m, 1 H, H^{5/8}), 7.96 (m, 1 H H^{5/8}), 7.64 (m, 1 H, H^{6/7}), 7.56 (m, 1 H, H^{6/7}), 7.44 (s, 1 H, H^{dithiolene}), 5.32 (s, 10 H, 2C₃H₃). Mass spectrum (CI): *m/z* 532 [Cp₂W(qedt)+H]⁺.

 $[Cp_2Mo(S_2C_2(Me)(pyridin-2-yl))]$ (11). CsOH·H₂O (147 mg, 0.87 mmol) was dissolved in anhydrous MeOH (5 cm³). 4-(Pyridin-2-yl)-5-(methyl)-1,3-dithiol-2-one (91 mg, 0.43 mmol) was added and the mixture stirred for 15 min and a brown solution was obtained. [Cp₂MoCl₂] (121 mg, 0.40 mmol) was then added and the mixture stirred overnight at room temperature. The solvent was then removed under a reduced pressure to yield a black solid. The solid was dissolved in CH₂Cl₂ and filtered through alumina; the alumina was washed with CH_2Cl_2 :MeOH (98:2) (3× 5 cm³) the washings combined and the solvent removed under a reduced pressure to give a brown solid. Column chromatography on alumina of the reaction mixture gave, on elution with CH₂Cl₂, the product as a single deep purple band which was collected and evaporated to dryness. The black solid was dissolved in a minimum volume of CH_2Cl_2 and *n*-hexane added until the product precipitated as a brown solid. The solvent was removed by decantation and the product dried under a reduced pressure. Yield 72 mg, 41%. Anal. Calcd. for C₂₀H₁₆MoN₂S₂: C, 53.07; H, 4.21; N, 3.44% Found: C, 54.08; H, 4.89; N, 3.29%. ¹H NMR (300 MHz, CDCl₃); δ 8.59 (m, 1 H, H⁶), 7.58 (m, 1 H, H³), 7.40 (m, 1 H, H⁴), 7.02 (m, 1 H, H⁵), 5.29 (s, 10 H, 2C₅H₅) 2.25 (s, 3 H, CH₃). Mass Spectrum (CI); $m/z = 409 [Cp_2Mo(S_2C_2(Me)(pyridin-2-yl)+H)]^+$.

Crystallography

Crystals containing each component of the $[1]^+/1$, $[3]^+/3$ redox couples; and $[8]^+$ and 9 were grown as described above. The details of the unit cell, data collection and refinement for the structures of 1, $[1][BF_4]$, 3, $[3][BF_4]$, $[8][BF_4]$ and 9 are given in Table 8. The structures were solved by either direct methods (1, $[1][BF_4]$, $[3][BF_4]$ and $[8][BF_4]$) or by heavy atom Patterson methods (3 and 9) using SHELXS97⁴² and refined by direct and difference Fourier methods using SHELXL97⁴² or teXsan⁴³ (for 3 only).

For 1, all of the non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at calculated positions and refined using a riding model. For [1][BF₄], one Cp ring was disordered over two sites, the major and minor occupancies being determined as 0.65 and 0.35, respectively; the disorder components were constrained to be regular pentagons. The F atoms were each disordered over two sites, the occupancies of which were constrained to sum to unity and the bonded and non-bonded distances of both fragments were constrained at chemically sensible values. The non-hydrogen atoms were refined anisotropically, with the exception of the disordered Cp ring and the minor [BF₄]⁻ site. Hydrogen atoms were included at calculated positions and refined using a riding model. For **3**, all of the non-hydrogen atoms were included at calculated positions but not refined.

For [3][BF₄], one Cp ring was disordered over two sites, each of occupancy 0.5. The F atoms were each disordered over two sites; the occupancy of one $[BF_4]^-$ group was set at 0.6 and the other at 0.4 and the bonded and non-bonded distances of both fragments were constrained at chemically sensible values. The non-hydrogen atoms were refined anisotropically, with the exception of the disordered Cp ring and the minor $[BF_4]^-$ site. Hydrogen atoms were included at calculated positions and refined using a riding model. All of the non-hydrogen atoms were included at calculated positions and refined using a riding model.

For $[8][BF_4]$ hydrogen atoms were included at calculated positions. The Cp ring C13 to C17 was disordered over two sets of sites, each with occupancy 0.5 and constrained to be a regular pentagon. The two disorder components were constrained to be regular pentagons. The atoms F3 and F4 were also each disordered over two sites, the occupancies of which were constrained to sum to unity. All non-hydrogen atoms were refined anisotropically, except those of the disordered Cp ring.

DFT Calculations

Restricted and unrestricted DFT calculations were performed using the Amsterdam Density Functional (ADF) suite version 2009.01.44,45 The DFT calculations employed a Slater-type orbital (STO) all-electron triple-ζ-plus one polarization function basis set from the ZORA/TZP database of the ADF suite for all atoms. The scalar relativistic (SR) approach was used within the ZORA Hamiltonian for the inclusion of relativistic effects and the local density approximation (LDA) with the correlation potential due to Vosko et al.46 was used in all of the DFT calculations. Gradient corrections were performed using the functionals of Becke⁴⁷ and Perdew (BP).⁴⁸ Models of $[1]^{z}$, $[6]^{z}$, 5 and 10 (z = 0, 1+ or 1-) in C_1 symmetry were constructed using geometrical data from the X-ray crystal structures of the available complexes. The coordinate frame employed in the calculations is shown in Fig. 9. In each model the z-axis bisects the S-M-S angle and the xaxis lies in the MS_2 plane (M = Mo, W). The model geometries were optimized at the ZORA SR level. For the unrestricted calculations pictorial representations of the MOs were generated using MOLEKEL⁴⁹ and fragment contributions to the MOs were obtained using Mulliken Population Analysis as implemented in the AOmix package.50,51

Summary and conclusions

The procedure reported previously by Davies *et al.*,^{22,23} *i.e.* the reaction of $[Cp_2MCl_2]$ (M = Mo or W) with the pro-ligand produced

by treating the corresponding R-1,3-dithiol-2-one with CsOH (Scheme 1), provides a convenient synthesis of $[Cp_2M(S_2C_2(H)R)]$ (M = Mo or W; R = phenyl, pyridin-2-yl, pyridin-3-yl, pyridin-4-yl or quinoxalin-2-yl) and $[Cp_2Mo(S_2C_2(Me)(pyridin-2-yl))]$. The availability of analogous Mo compounds with a variety of substituents on the dithiolene group and their W counterparts has allowed informed comparisons to be made concerning their nature and properties.

Electrochemical and associated UV/vis/NIR spectroelectrochemical investigations have shown that each of these $[Cp_2M(S_2C_2(H)R)]$ compounds in dmf has a rich redox chemistry; thus, each compound undergoes two, and in some cases three, oxidations and reductions. For each compound the first oxidation (OX^i) is both electrochemically and chemically reversible and the one-electron reduction (RED¹) is electrochemically reversible; the latter process is chemically reversible for the Mo but not for the W compounds. Each redox change occurs at a more positive potential for a Mo compound than for its W counterpart; typically, $\Delta \approx 30$ and 300 mV for OX¹ and RED¹, respectively.

DFT calculations have provided valuable information concerning the electronic structure of the parent compounds and their mono-cations and mono-anions. OX1 involves the removal of an electron from an orbital that is primarily dithiolene C-C π -bonding and C-S π -antibonding in character. This information is consistent with the EPR spectra of the Mo monocations, in that each manifests coupling of the unpaired electron with the dithiolene H atom (or for $[11]^+$ $[Cp_2Mo(S_2C_2(Me)(2-Me)(S_2C_2(Me)(S_2(Me)(S_2C_2(Me)(S$ pedt))]⁺ the three H atoms on the Me group) and a relatively small ^{95,97}Mo hyperfine coupling. Also, the results of crystallographic studies accomplished for both components of the $[Cp_2Mo(S_2C_2(H)R)]^+/[Cp_2Mo(S_2C_2(H)R)]$ (R = Ph or pyridin-3yl) redox couples show changes in the length of the Mo-S, S-C and C-C bonds of the {MoSCCS} moiety that are generally consistent with OX¹ involving the loss of an electron from an orbital that is Mo-S and C-S antibonding and C-C bonding in character.

The DFT calculations indicate that the unpaired electron is more localised on the metal in mono-anions than in the monocations. The EPR spectrum of the each Mo containing monoanion manifests a larger ^{95,97}Mo coupling than observed for the corresponding mono-cation. Also, each redox change occurs at a more positive potential for a Mo compound than for its W counterpart; typically, $\Delta \approx 30$ and 300 mV for OX¹ and RED¹, respectively.

 $[Cp_2W(S_2C_2(H)(quinoxalin-2-yl))]$ (10) is notable in respect of the potential and nature of RED¹. Thus, the potential of RED¹ for 10 is *ca.* 230 mV more positive than expected from that of its Mo counterpart and the EPR spectrum of $[10]^-$ is typical of an organic radical. DFT calculations show that these properties arise because RED¹ involves the addition of an electron to a quinoxalin-2-yl π orbital.

The studies reported herein clearly demonstrate that: (1) The nature of the substituent(s) of a dithiolene ligand modulate the properties of the complex, including the potential at which redox changes occur. (2) Proton addition to a substituent possessing a basic site, such as a heterocyclic nitrogen atom, provides a further means of modulating the potential at which redox changes of the complex occur. (3) As shown by the nature of RED¹ for **10**, the redox chemistry of a dithiolene complex can be inherently that of a substituent. Given the extended functionality of molybdopterin,⁵

we consider that these three points are relevant to the quest of understanding the role of this cofactor in the catalyses accomplished at the Mo (and W) centres of the oxotransferase enzymes.

Acknowledgements

We thank the EPSRC for financial support, including the facilities and expertise provided by the EPSRC EPR National Service, and Professor Lesley Yellowlees of Edinburgh University for access to NIR spectroelectrochemical facilities.

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