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Synthesis and characterisation of Mo^{IV}-oxo dithiolenes: formate dehydrogenase active site mimetics

Isaac J. Furney† and Joseph A. Wright  *

The active sites of metalloenzymes continue to inspire synthetic chemists to create structural models of the intricate structures seen in biology. As well as the fundamental intellectual challenge, this is driven by the potential societal impact that many of these systems offer. Formate dehydrogenases (FDHs) hold such potential: formate is one of the key candidates as a hydrogen carrier for future energy transport. Efforts at mimicking the active site of FDH require the synthesis of (functionalised) molybdenum bis(dithiolene) complexes, principally featuring the Mo=O unit. In this review, we give an overview of the synthetic routes used to date in these efforts, along with key infrared and electrochemical data for the full collection of synthetic complexes reported to date.

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1 Introduction

The industrial application of fossil fuels has provided humanity with an abundant source of materials and energy. Unfortunately, the limited supply and negative environmental effects require alternatives to be found. Many exist, for example, wind or solar, but none match the properties of the currently available petroleum infrastructure as well as hydrogen. Hydrogen has a large gravimetric energy density, greater than conventional fossil fuels, but unfortunately a poor volumetric energy density.¹ The oxidation of hydrogen yields water and therefore is not as environmentally damaging as the fossil fuel oxidation by-products.

Hydrogen can be generated by the electrolysis of water but requires electrocatalysts that themselves often rely on precious metals such as platinum and iridium. The storage and transportation of hydrogen is also an issue stemming from the risk of explosion. This risk is exacerbated as hydrogen, due to its size and reactivity, can penetrate metals, compromising their structural integrity.²

To circumvent these issues whilst retaining the benefits of hydrogen as a fuel, carrier molecules are an attractive solution. The ideal carrier molecule will be small, dense, air stable and non-toxic. Water, perhaps the molecule which meets these criteria best, is, as already detailed, unsuitable for this role. As a result, various other liquid organic hydrogen-carrying molecules

(LOHCs) have been explored. The formate anion (HCOO[−]) has a hydrogen density of 53 g L^{−1}, 590 times that of gaseous hydrogen. This anion can also serve as a feedstock for other chemicals that are largely reliant on fossil fuel production, such as methanol. The ability of formate to double as both a hydrogen carrier and a chemical building block makes it a prime candidate in the LOHC space, as is the potential to utilise both formic acid and formate, *i.e.* either liquid or solid carriers. Unfortunately, producing formate is a thermodynamically unfavourable process, so current methods must be improved towards catalytic means.³

The challenge in exploiting the potential of formate is in producing it cleanly and with high energy efficiency. Electroreduction of carbon dioxide is possible, but existing chemical routes sacrifice either energy efficiency (overpotential) or selectivity (dihydrogen release) in order to achieve this. Nature has already solved this conundrum: the formate dehydrogenase (FDH) enzymes can reversibly interconvert CO₂ and formate selectively, without requiring energy-intensive high overpotentials and using only Earth-abundant elements.⁴ Unfortunately, there are significant downsides to using the enzymes: they are extremely oxygen sensitive and their size limits currents both in solution and when immobilised on surfaces. Whilst this rules out using the FDH enzymes themselves as practical electrocatalysts in real-world devices, the possibility of creating functional formate-producing catalysts by mimicking these natural systems is extremely attractive.

Here, we examine enzymatic structures that provide the inspiration for this work, the challenges in the synthesis and the results to date in producing Mo^{IV}=O dithiolene moieties. These structures are the core of the FDH enzyme and access to a variety of such systems is likely a prerequisite for accessing catalytically-competent biomimetics with useful overpotentials.

School of Chemistry, Pharmacy and Pharmacology, University of East Anglia, Norwich NR4 7TJ, UK. E-mail: joseph.wright@uea.ac.uk

† Isaac J. Furney obtained a first class Masters in Chemistry from the University of East Anglia in 2021, writing his Masters dissertation on novel CO₂-to-formate catalysis. He then began his Ph.D., further developing the work he had started in his Masters.

2 Molybdoenzyme active site structure

To date, more than 50 different types of molybdoenzymes have been identified, and they can be classified into four families according to their protein sequences and the structure of the active site: xanthine oxidases, sulfite oxidases, dimethyl sulfoxide (DMSO) reductases and nitrogenases.⁵ Other than the nitrogenases (which are not considered further in this review), these enzyme families exhibit significant active site similarity and a wide scope of roles.^{6–10} In particular, they feature a single molybdenum atom in their active site ligated by at least one dithiolene, which is found as part of a pyranopterin cofactor (Fig. 1).

2.1 Formate dehydrogenases

Formate dehydrogenases (FDHs) belong to the DMSO reductase family of enzymes. The FDH subgroup can be further divided into two categories: metal-dependent and metal-independent (NAD-dependent). In common with the rest of the DMSO reductase family, the FDH subgroup is identifiable by having two pyranopterin ligands leading to a square-based pyramidal geometry at the metal. One or two oxygen, sulfur, or selenium atoms complete the coordination sphere (Fig. 2). There are also tungsten-containing FDH enzymes, which exhibit similar structures.¹¹ In total, three formate dehydrogenase enzymes have been characterised by X-ray crystallography: two molybdenum-based^{12,13} and one tungsten-based.¹⁴

As well as the intrinsic synthetic challenge and potential technological applications, synthetically modelling the FDH active site is attractive, as it may help in unravelling the reaction mechanism employed by the enzyme. To date, five poss-

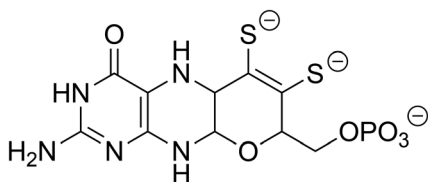


Fig. 1 The pyranopterin cofactor.

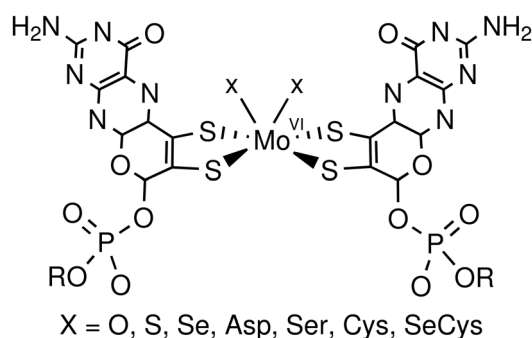


Fig. 2 The DMSO reductase active site.¹⁵

ible mechanisms have been suggested, and so far no consensus has been reached on key aspects.^{12,14,16–19} Structures containing the Mo=O functionality are of particular interest due to the demonstration of catalysis in a synthetic mimic containing this metal structure.²⁰

3 Synthesis of biomimetic Mo=O structures

The synthesis of biomimetic molybdenum dithiolenes began with Donahue and Holm in the 1990s with their succinylt ligands named edt (1), bdt (2) and mnt (3) ligands with a variety of analogous complexes based on changing the functionality at the terminal position (Fig. 3).²¹ Like most inorganic syntheses, the creation of these biomimetic complexes can be broken down into two parts: the prolignand synthesis, with an emphasis on dithiolene insertion, and subsequent complexation.

3.1 Dithiolene precursor synthesis

Many methods exist to achieve the introduction of dithiolenes into the coordination sphere. However, this review focuses on those methods suitable for use in systems exceeding a few carbons, for example, Holm's landmark edt, bdt and mnt ligands, which are built from feedstock chemicals such as NaCN and CS₂.^{21–23} These methods focus on the creation of suitable precursor molecular structures in the first stage. Given the general sensitivity of the ene-1,2-dithiolate moiety, most research groups have protected this unit until coordination to the metal is attempted, either by retaining it in the form of a dithione derivative or using an ester protecting group. The key methods used are summarised in Fig. 4.

In method 1, a trithiocarbonate precursor was synthesised by reaction of a symmetrical alkyne with ethylene trithiocarbonate under reflux (this can also be performed using ultraviolet light).^{31,32} The trithiocarbonate was then oxidised using mercury acetate and acetic acid to give the oxo-dithiocarbonate/dithione.²⁴

In a variant of this approach, Ried and coworkers demonstrated that the addition of CS₂ and elemental sulfur to an alkyne generated a trithiocarbonate moiety; subsequent oxidation to the dithione was encouraged through the addition of sulfuric acid (method 2).²⁵

Fontecave and coworkers developed a route to their novel protected dithiolene ligand by subjecting a bromovinyl triflate

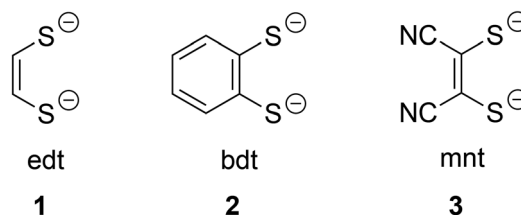


Fig. 3 The early ligands of Donahue and Holm.²¹

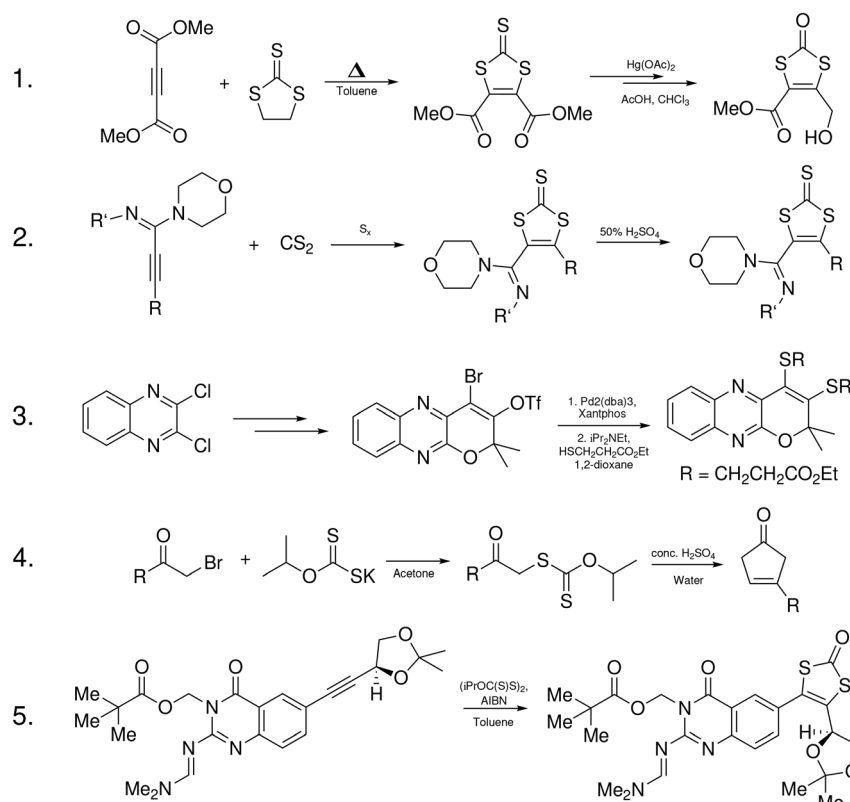


Fig. 4 The synthetic routes developed by various groups to access the dithione/dithiolene moiety. Methods 1,²⁴ 2,²⁵ 3,²⁶ 4,²⁷ 5.^{28–30}

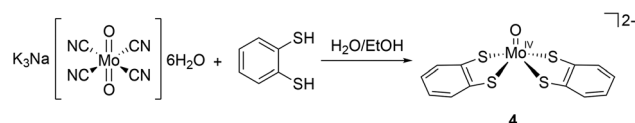
to a double palladium-catalysed cross-coupling reaction with two equivalents of $\text{HSCH}_2\text{CH}_2\text{CO}_2\text{Et}$ (method 3).^{20,26}

Hortmann and coworkers developed a method to achieve the dithione moiety starting from the addition of bromoacetyl analogues to potassium isopropyl xanthate, where eventual cyclisation was encouraged by a strong acid (method 4).²⁷

Although a method that has not been employed to introduce dithiolene ligands in their proligand form to molybdenum-oxo dithiolene complexes, Gareau and coworkers showed that through the radical cyclised addition of diisopropyl xanthogen disulfide, an alkyne functionalised moiety, the dithione group can be inserted.²⁸ This insertion method was utilised by Garner and Joule to develop a proligand that after further synthesis gave a ligand of remarkable similarity to the pyranopterin ligand (method 5).^{29,30} It does not appear to have been complexed with molybdenum to generate the biomimetic species.

3.2 Complexation

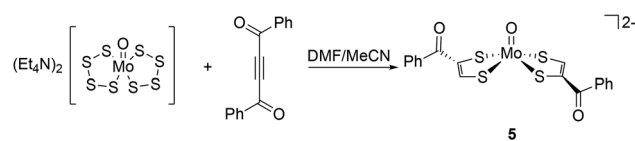
Complexing these ligands to molybdenum can follow a variety of routes from direct coordination to a molybdenum precursor (for example $\text{MoO}_2(\text{CN})_4^{3-}$ or MoOCl_5^{2-}) (Scheme 1) or by transmetallation from a nickel intermediary. Obtaining the latter complexes is relatively straightforward when the ligand scaffold is unfunctionalised, as in the case of edt (1) and mnt (3). Synthetic difficulty increases according to the complexity of the ligand.²¹



Scheme 1 The synthesis of $[\text{MoO}(\text{bdt})_2]^{2-}$ (4) by Holm and Donahue.²¹

Some groups have found success implementing a post-coordination functionalisation approach in which the dithiolene scaffold is constructed first and then, by the addition of a substituted alkyne, additional functionality is deposited onto the complex (Scheme 2).^{33–35} However, this method is highly dependent on the activating nature of the alkyne.

Fig. 5 summarises all molybdenum-oxo bis(dithiolene) complexes synthesised to date. Most of these structures are limited in biomimetic features beyond the primary coordination sphere. Therefore, further synthesis directed toward



Scheme 2 The post-coordination functionalisation synthesis of complex 5 employed by Sarkar and coworkers.³⁴

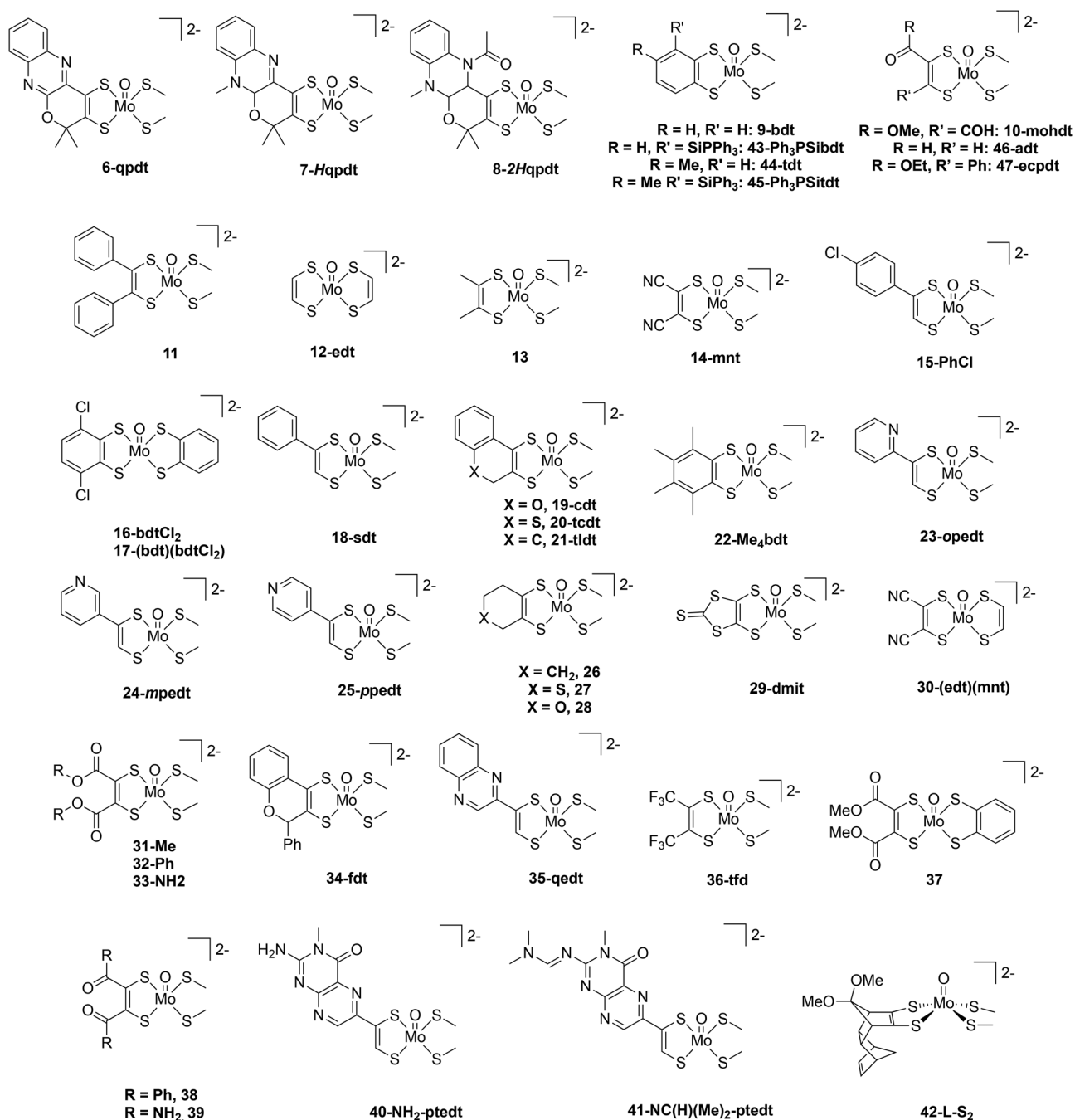


Fig. 5 Mo^{IV}O(dithiolene)₂ complexes reported to date.^{20,21,23,24,26,33–44}

individual components of the cofactor is likely to be productive in the identification of the most important features for the natural system.

4 Spectral and electrochemical properties

Table 1 enumerates the key data for the Mo=O complexes where electrochemical data have been reported, along with the

Mo=O stretching frequency where available. The infrared data are readily compared directly from the primary literature. Notably, almost all of the values lie around 900 cm⁻¹ independent of the (formal) oxidation state of the metal centre. This is unaffected by ligation (see below) and shows no pattern in the values.

However, for the electrochemical potential, a direct comparison is more challenging due to variations in solvent and internal reference in the original reports. Work by Addison and coworkers allows one to convert between the different

Table 1 Spectroscopic and electrochemical properties of molybdenum-oxo bis(dithione) complexes

Complex	M=O stretch $\tilde{\nu}/\text{cm}^{-1}$	Supporting electrolyte	Solvent	Reference	$E_{1/2}/\text{V}^a$	
					$\text{Mo}^{\text{IV}}/\text{Mo}^{\text{V}}$	$\text{Mo}^{\text{V}}/\text{Mo}^{\text{VI}}$
6-qpdt ²⁶	905	Bu ₄ NOCl	MeCN	Ag/AgCl/KCl sat	−0.617	0.123 ^b
7-Hqpdt ²⁰	901	Bu ₄ NOCl	MeCN	Ag/AgCl/KCl sat	−0.767	−0.027 ^b
8-2Hqpdt ²⁰	925	Bu ₄ NOCl	MeCN	Ag/AgCl/KCl sat	−0.937	−0.127 ^b
9-bdt ²¹	903	Bu ₄ NPF ₆	MeCN	SCE	−0.77	0.18
10-mohbdt ²⁴	925	Bu ₄ NPF ₆	MeCN	Fc/Fc*	−0.62	
11 ⁴⁶	903 ^b	Bu ₄ NPF ₆	MeCN	SCE	−0.89	−0.13
12-edt ²¹	917	Bu ₄ NPF ₆	MeCN	SCE	−0.99	^c
13 ⁴⁶	889	Bu ₄ NPF ₆	MeCN	SCE	−1.04	−0.27
14-mnt ²¹	928	Bu ₄ NPF ₆	MeCN	SCE	0.1	^c
16-bdtCl₂ ⁴²	910	Bu ₄ NPF ₆	MeCN	SCE	−0.48	^c
17-(bdt)(bdtCl₂) ³³	907	Bu ₄ NPF ₆	MeCN	SCE	−0.61	
18-sdt ³⁷	879	Bu ₄ NPF ₆	DMF	SCE	−0.86	^c
19-cdt ³⁶	905	Bu ₄ NPF ₆	—	Fc/Fc*	−0.72	
20-tcdt ³⁶	—	Bu ₄ NPF ₆	—	Fc/Fc*	−0.87	
21-tldt ³⁶	—	Bu ₄ NPF ₆	—	Fc/Fc*	−0.95	
22-Me₄bdt ¹¹	—	Bu ₄ NPF ₆	MeCN	SCE	−0.91	−0.54 ^b
23-opedt ³⁷	902	Bu ₄ NPF ₆	DMF	SCE	−0.8	
24-mpedt ³⁷	882	Bu ₄ NPF ₆	DMF	SCE	−0.77	^c
25-ppedt ³⁷	900	Bu ₄ NPF ₆	DMF	SCE	−0.73	
26 ⁴³	896	Bu ₄ NPF ₆	MeCN	SCE	−0.94	−0.19
27 ⁴³	899	Bu ₄ NPF ₆	MeCN	SCE	−0.95	−0.20
28 ⁴³	902	Bu ₄ NPF ₆	MeCN	SCE	−1.08	−0.32
29-dmit ⁴⁰	930	Bu ₄ NOCl	MeCN	SCE	−0.26	0.14 ^b
30-(edt)(mnt) ²¹	919	Bu ₄ NPF ₆	MeCN	SCE	−0.46	0.16 ^b
31 ³⁵	914	Bu ₄ NOCl	MeCN	Ag/AgCl/KCl sat	−0.457	0.393 ^c
34-fdt ⁴¹	1017	Bu ₄ NPF ₆	MeCN	Fc/Fc*	−1.33	−0.04 ^c
35-qedt ³⁷	905	Bu ₄ NPF ₆	DMF	SCE	−0.66	
36-tfd ²¹	—	Bu ₄ NPF ₆	MeCN	SCE	−0.2	0.26 ^b
37 ³³	908	Bu ₄ NPF ₆	MeCN	SCE	−0.62	
38 ³⁴	950	Et ₄ NOCl	MeCN	SCE	−1.22 ^c	^c
40-NH₂-ptedt ³⁷	886	Bu ₄ NPF ₆	DMF	SCE	−0.73	
42-NC(H)(Me)₂-ptedt ³⁷	890	Bu ₄ NPF ₆	DMF	SCE	−0.71	
42-L-S₂ ²¹	890	Bu ₄ NPF ₆	MeCN	SCE	−1.09	−0.34
43-PPh₃Sibdt ²³	915 ^b	Bu ₄ NOCl	DMF	SCE	−0.79	
44-tdt ²³	900 ^b	Bu ₄ NOCl	DMF	SCE	−0.83	
45-PPh₃Sitdt ²³	906 ^b	Bu ₄ NOCl	DMF	SCE	−0.84	0.14
46-adt ⁴⁴	936	Bu ₄ NPF ₆	MeCN	SCE	−0.87	
47-ecpdt ⁴⁴	929	Bu ₄ NPF ₆	MeCN	SCE	−0.52	

^a The redox couples have been standardised to the Fc/Fc* redox couple. ^b Quasi-reversible wave. ^c Irreversible wave.

referencing methods;⁴⁵ this adjustment is determined in acetonitrile, and therefore work in other solvents is likely subject to more uncertainty.

Table 1 illustrates how strongly ligation affects the electrochemistry of these molybdenum-oxo dithiolene complexes. The Mo^{IV}/Mo^V redox couple is well documented and is reversible for all complexes except for **38**. In contrast, the Mo^V/Mo^{VI} redox couple is much more poorly documented, with a range of reported behaviours. It has been reported as quasi-reversible for six systems and reversible for seven. Looking at the ligands and comparing them with each other offers some commonalities in the scaffolds (Fig. 5). The ligands supporting complexes with reversible behaviour are usually ‘simple’: alkyl and aryl substituents which lack adjacent functionality. In contrast, those with quasi-reversible behaviours feature more intricate ligands which likely undergo more significant rearrangement in solution on oxidation.

There are two general trends linking ligand structures and redox values. First, the alkyl/aryl-substituted systems that lack

electron-withdrawing groups and thus exhibit higher redox potentials. Secondly, the more reducing a ligand is, the more negative the redox potential, as seen, for example, in the work of Fontecave and coworkers.^{20,26}

5 Catalysis

Of the above biomimetic structures of the FDH active sites, only the complexes created by Fontecave and coworkers, **5–7**, have exhibited an ability to photocatalytically reduce carbon dioxide to formate, following the methodology presented by Ishitani and coworkers.^{20,26,47,48} Compound **6** had the highest cumulative TONs followed by **8** and then **7**. Interestingly, the reverse is true for complexes with the most CO₂ derived reduction products, that being **8**, **7**, and **6**.

Several of the remaining molybdenum-oxo bis(dithiolene) complexes have had their oxygen atom transfer catalytic ability investigated. Oku and coworkers determined the influence

sterics has on **tdt** and **bdt** coordinated systems through their novel silyl-substituted dithiolene ligands.²³ Upon addition of Me₃NO to both **9** and **43**, the bulkiness of the Ph₃Si group significantly decreased the rate constant of MoO₂ formation. Schulzke and coworkers investigated the oxygen atom transfer (OAT) catalysis of their novel complex **10** by using the model OAT reaction developed by Berg and Holm in 1985 to investigate MoO₂ (LNS₂)-type systems.^{24,49} The reaction involves the OAT from dimethylsulphoxide (DMSO) to the catalyst and then to an acceptor such as triphenylphosphine (PPh₃) to give triphenylphosphine oxide (PPh₃O). The reaction proceeded very slowly with a maximum conversion of 93% over approximately 60 hours. When trimethylamine *N*-oxide (Me₃NO), a stronger oxidiser, was used instead of DMSO, there was a 37% conversion of PPh₃O in 15 hours. Through the use of UV/VIS spectroscopy, Schulzke reasoned that the inert Mo^V₂O₃ species was forming, resulting in the slow times recorded, possibly encouraged by the presence of hydrogen bonding groups on **10**.

Drawing mechanistic conclusions from the above catalytic experiments to aid future ligand design is difficult because of the lack of further testing of the complete catalogue of complexes. It is important to bear in mind that other research groups have found more interest in characterising OAT ability of the oxidised analogue of their complexes (Mo^{VI}O₂) rather than the reduced species (Mo^{IV}O).^{38,43,50–52} One could assume that the lack of catalytic results implies that those systems were in fact not active; this is especially true with regard to carbon dioxide reduction. For OAT catalysis, some primary conclusions can be drawn: steric bulk impedes MoO₂ formation and hydrogen bonds encourage dimerisation through a bridging oxygen.

6 Summary and outlook

Over the roughly 40 years since the first recorded deliberate synthesis of a molybdenum-oxo bis(dithiolene) complex, progress in understanding these biomimetic systems has been slow, likely because of how synthetically challenging access to these systems is. However, this and similar areas of research will see increased interest in the coming years as the financial and social incentive to procure viable fossil fuel alternatives becomes more pressing. Early Mo^{IV}O(dithiolene)₂ structures focused around the core dithiolene unit, lacking any real functionality on the vinyl carbons. Like with all things, advances in synthetic organic chemistry as a function of time have allowed for more interesting ligand scaffolds with recent designs resulting in the first series of complexes to show photocatalytic carbon dioxide reduction to formate. With a greater ease of procuring new novel proligands and subsequent small-molecule mimics, one's ability to better understand the catalytic mechanism behind FDH grows with each passing year. However, incomplete characterisation and a lack of standardisation of techniques between research groups make comparing catalytically-successful complexes difficult.

Very recent work on related tungsten systems suggests that there is significant untapped potential in this area.⁵³ Even

unfunctionalised ligands may offer the potential for catalysis, and one may anticipate that as more complex architectures become available, advances in electrocatalysis using Mo=O dithiolenes will increase markedly.

Author contributions

JAW conceptualised the research topic. IF carried out investigation to collect the literature data. IF and JAW wrote the paper jointly.

Data availability

No new data are presented in the manuscript: they are all taken from the primary literature.

Conflicts of interest

There are no conflicts to declare.

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