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Reactivity of a Biomimetic W(IV) Bis-Dithiolene Complex with CO_2 Leading to Formate Production and Structural Rearrangement

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A mononuclear W(IV) bis-dithiolene complex stabilized by an oxo ligand exhibits a reductive reactivity toward CO_2, from which formate and a dinuclear W(V) complex are generated. An unusual structural rearrangement was observed during the reaction. Structural and spectroscopic characterizations for a novel triply bridged dinuclear W(V) complex are reported.

In the current energy system using the fossil fuels, the utilization of CO_2 obtains substantial research interests because the conversion of the combustion waste to valuable industrial products can decrease the emission of the unwanted gas to the air.[1-4] The science and technology for the CO_2 capture and conversion are continually developing, although the poor reactivity of CO_2 makes the chemical transformation quite challenging. Considerable efforts have been made to develop transition-metal based catalysts and electrocatalysts for the CO_2 conversion,[3, 5] among which tungsten complexes have shown versatile reactivity.[6-12] Selected examples include the low-valent tungsten complex to form a W-CO_2 adduct such as μ_2-η^3 type W-CO_2-Li in the presence of Lewis acid,[13] a zero-valent tungsten phenoxide to form phenyl carbonate via a reversible insertion of CO_2,[14] and a tungsten carbonyl complex to generate a tungsten hydrido-carbonate or hydrido-carbamate from CO_2 with excess methanol or secondary amine.[15] Additionally, a tungsten-hydride $HW(CO)_5^-$ is known to react with CO_2 to produce formate.[16]

In nature, there exist tungsten containing formate dehydrogenases (W-FDHs) that reversibly convert formate to CO_2 (formate $\rightleftharpoons$ CO_2 + H^+ + $2e^-$) (Figure 1).[17] Unlike the aforementioned synthetic CO_2-activating complexes, the tungsten ion in the W-FDH remains in high valencies, alternating the +4 and +6 oxidation states during the catalytic cycle. Hirst *et al.* reported the purified Mo/W-FDH proteins exhibited superb electrocatalytic activity, in which the conversion of CO_2 to/from formate was achieved around the thermodynamic potential (–0.49 V vs. NHE).[18, 19]

The W centre in the FDH is stabilized by two redox non-innocent pyranopterin dithiolate ligands (Figure 1).[17] A group of bis(dithiolene)tungsten FDH model complexes that closely imitate the enzyme active site structure have been synthesized.[20] There also is a reported model complex for the formate-bound form, $[WO(HCO_2)(S_2C_2Me_2)_2]^-$.[21] The most studied chemical reactivity of the FDH model complexes is an oxygen atom transfer (OAT) chemistry.[22] Holm *et al.* reported that $[W^{IV}O(S_2C_2Me_2)_2](Et_4N)_2$ (**1**) undergoes OAT with trimethylamine N-oxide (Me_3NO) to yield Me_3N and the corresponding dioxo species, $[W^{VI}(O)_2(S_2C_2Me_2)_2](Et_4N)_2$.[23] Majumdar *et al.* reported a similar OAT of $[W^{IV}O(S_2C_2(CN)_2)_2]^{2-}$ using the Me_3NO.[24] Sarkar *et al.* showed $[W^{IV}O(S_2C_2(CN)_2)_2]^{2-}$ reacts with HCO_3^- to give $[W^{VI}(O)_2(S_2C_2(CN)_2)_2]^{2-}$ and HCO_2^- in aqueous media.[25] In addition to the OAT, complex **1** can be oxidized by iodine to form a one-electron oxidized analogue, $[W^VO(S_2C_2Me_2)_2]^-$.[23] However, the enzyme-like CO_2/formate conversion has not been reported with these FDH model complexes to date.

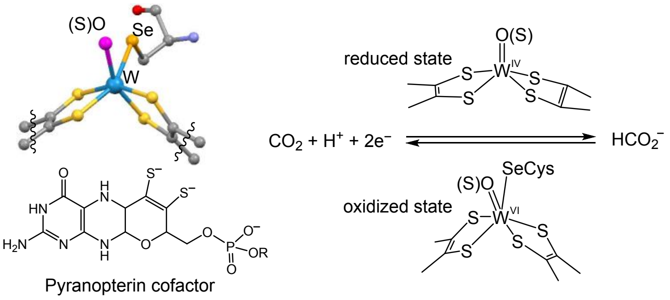

Figure 1. (left) Active site structure of the W-FDH in the oxidized state (*Desulfovibrio gigas*, PDB ID: 1H0H); (right) the reversible conversion of CO_2 to formate catalysed by the active site.

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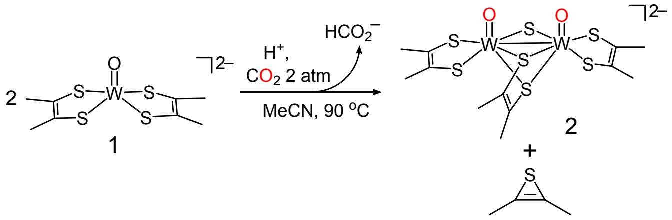
We have investigated the reactions between W(IV) bis-dithiolene complexes and gaseous CO_2. In the previous isotopic labelling experiments,[26] we observed that a biomimetic bis-dithiolene W^{IV}-OH species reacted with CO_2 to form a W-(bi)carbonate intermediate indicating a direct interaction between the high-valent W^{IV} centre and the oxygen of gaseous CO_2.[26] This was encouraging because a computational study suggested that a M-thiocarbonate intermediate could form prior to the generation of the M-formate (M = Mo, W) during the catalytic cycle of the FDHs,[27] although another pathway of leaving a thiocarbonate moiety as attached in the cysteine residue has been proposed elsewhere.[28] However, our previous model system did not proceed with the following reduction step to form formate or other reduced CO_2 species.[26] Here, we report the CO_2 reactivity of the bis(dithiolene) W^{IV}=O complex, which leads to the generation of formate at elevated temperatures (e.g., 90 °C). Our efforts to investigate the thermal reactivity of this complex was inspired by the natural conditions, in which the W-FDHs thrive at hydrothermal vents. Although there has been a report on the correlation between temperature and electrochemical behaviours of the Mo- or W-dithiolene complexes,[29] the temperature-dependent chemical reactivity of the FDH model complexes has not been reported.

A W^{IV} bis-dithiolene complex stabilized by an oxo ligand, $[W^{IV}O(S_2C_2Me_2)_2]^{2-}$ (**1**), is quite robust even at elevated temperatures in solution. No sign of decomposition was observed when **1** was heated in acetonitrile at 90 °C under Ar over several days. When an acetonitrile solution of **1** was exposed to gaseous CO_2 (2 atm) at room temperature, **1** did not show any reactivity even after several days. However, changing the reaction temperature to 90 °C completely converted **1** to a new, unexpected dinuclear complex, $[W^V_2O_2(\mu\text{-}S)(\mu\text{-}S_2C_2Me_2)(S_2C_2Me_2)_2](Et_4N)_2$ (**2**) over 4 days (scheme 1). The product **2** was isolated in 86 % yield as an orange solid. The **1**-to-**2** conversion was accompanied by an asymmetric bond cleavage of the W-S and C-S bond in one of the dithiolene ligands, leaving a dimethylthiirene fragment as another reaction product, which was detected by GC-MS (Figure S1). This type of dithiolene ligand cleavage has never been reported previously. Along with the oxidative conversion of **1** to **2**, remarkably, a gaseous CO_2 was reduced by two electrons to form formate (HCO_2^-) (*vide infra*).



Scheme 1. Structural rearrangement of a mononuclear W complex $[W^{IV}O(S_2C_2Me_2)_2](Et_4N)_2$ (**1**) to a dinuclear $[W^V_2O_2(\mu\text{-}S)(\mu\text{-}S_2C_2Me_2)(S_2C_2Me_2)_2](Et_4N)_2$ (**2**) under CO_2 atmosphere along with a concomitant reduction of CO_2 to formate .

X-ray analysis of the single crystal of **2** reveals a triply bridged dinuclear tungsten centres by a *μ*-sulfide and a *μ*-dithiolene ligand (Figure 2). Each W centre is in a distorted octahedral geometry. The W–W distance of 2.823(8) Å and the small W1–S–W2 angle (68.18°) suggest a direct metal-metal interaction. DFT calculation supports the W–W bond in the ground state, where the d_{xy} orbitals of the two tungstens in the HOMO level overlap very well due to the high degree of symmetry (Figure S2). The W–W bond distance is considerably shorter by ~0.2 Å than a doubly bridged W---W (3.000 Å) distance of the $[W^V_2(\mu_2\text{-}S)_2(S_2C_2Me_2)_4]^{2-}$ complex.[23] Each W^V=O bond (~1.72 Å) of **2** is in a typical range of W^V=O bond distance.[30] The quasi-symmetric W^V=O bonds of **2** in the *syn* conformation exhibit a strong infrared stretch frequency at 918 cm^{-1}, which is 23 cm^{-1} higher than that of the W^{IV}=O (895 cm^{-1}) of **1** (Figure S3). The peripheral dithiolate ligand coordinates to the W ion asymmetrically. The W1–S5 bond *trans* to the *μ*-S7 is measured 0.024 Å longer than the W1–S6 bond, and the similar trend is observed in the W2 centre (W2-S1 2.399(2); W2-S2 2.422(3) Å). Strong *trans* influence is observed in the *μ*-dithiolate ligand, where the W–S4 bond *trans* to the W=O is elongated severely by 0.24 Å in comparison to the W–S3. The bridging and peripheral dithiolate ligands were also distinguished in the solution NMR spectrum. The ^{13}C NMR (CD_3CN) spectrum of **2** exhibits two sets of the dithiolates (Figure S4).

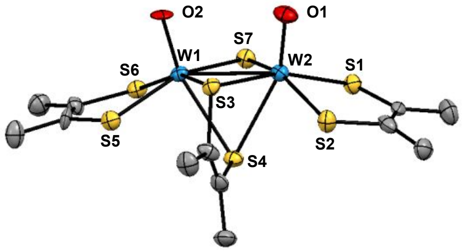


Figure 2. Molecular structure of $[W_2O_2(\mu\text{-}S)(\mu\text{-}S_2C_2Me_2)(S_2C_2Me_2)_2]^{2-}$ (**2**) with 50 % probability ellipsoids. Counter ions ($2Et_4N^+$) and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows: W1–O2 1.722(6), W2–O1 1.712(7), W1–S3 2.478(2), W1–S4 2.730(2), W1–S5 2.427(2), W1–S6 2.403(2), W1–S7 2.374(2), W2–S1 2.399(2), W2–S2 2.422(3), W2–S3 2.489(2), W2–S4 2.713(2), W2–S7 2.382(2), W1–W2 2.823(8), W1–S3–W2 69.26(6), W1–S7–W2 72.80(6), W1–S4–W2 62.48(5).

Redox non-innocent dithiolene is interconvertible among three possible oxidation levels, ene-1,2-dithiolate $(S_2C_2R_2)^{2-}$ ↔ thienyl radical anion $(S_2C_2R_2)^{-\bullet}$ ↔ 1,2-dithione.[31, 32] The dithiolene ligand of **2** can be identified by measuring the dithiolene backbone distances.[33] The C–C (1.32–1.35 Å) and the C–S (1.75–1.80 Å) bond distances of the bridging and peripheral dithiolene in **2** suggest the fully reduced dithiolates.[33] Accordingly, the oxidation states of both of the W ions are assigned as W^V state. The S K-edge X-ray absorption spectrum and the complementary simulation data suggest relatively low covalency of the W d-orbital with the p orbital of S from the dithiolene, and moderate S-character is observed in the bridging sulfide (Figure S5). It is due to the relative hardness of the W^V ion.

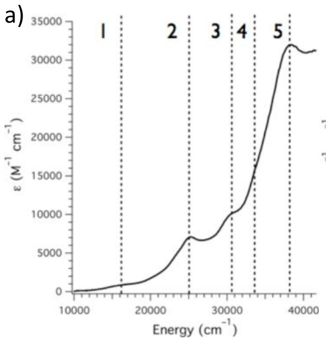


Figure 3. (a) Experimental, and (b) simulated absorption spectra of the complex **2**. The prominent transitions (1 – 5) are assigned from the TD-DFT calculations (Figure S6).

The orange-yellow solution of **2** in acetonitrile exhibits distinctive UV-Vis absorption features at 261 (ϵ = 32,000), 299 (sh, 16,100), 328 (9,800), and 396 (7,100) nm (Figure 3a). We assigned the transitions using TD-DFT (time-dependent density functional theory) calculations. A simulated spectrum (Figure 3b) indicates that absorption bands are dominated by the ligand-to-metal charge transfers (LMCTs). The strong bands at 261 nm and the 299 nm correlate with S⟶W charge transfer. The 328 nm band is from μ-dithiolene⟶W charge transfer, and the band at 396 nm relates with the peripheral dithiolene⟶W charge transfer. (Figure S6).

Conversion of complex **1** to **2** occurred only when the reaction solution was incubated under the CO_2 atmosphere (Figure 4a ⟶ 4b). This implies a concomitant reduction of the CO_2 gas. Complex **2** itself does not contain any CO_2-originated carbon. However, we were able to observe a strong peak at 1640 cm^{-1} in the IR spectrum of the crude reaction product, which suggests a presence of a CO_2-derived product (identified as a formate, Figures 4c). To confirm the origin of the 1640 cm^{-1} peak, we used the isotopically labeled $^{13}CO_2$ gas under the same reaction conditions. The IR spectrum of the isotope reaction products showed a new peak at 1595 cm^{-1} along with abolishment of the 1640 cm^{-1} peak (Figure 4c). The 45 cm^{-1} wavenumber shift clearly indicates the participation of the CO_2 in the reaction. Next, we identified the CO_2-derived product by comparing its ^{13}C NMR spectrum with that of Et_4NHCO_2 in acetonitrile (Figure S7). Both spectra of the reaction product and the formate standard gave rise to a ^{13}C NMR peak at 164 ppm, confirming that product of CO_2 reaction with **1** is the formate (Figure S8). In a further analysis, the crude reaction solution was treated with ~10 equiv. of HCl (diluted in 1,4-dioxane) in order to protonate the formate. Inspection of the solution with GC-MS (gas chromatography-mass spectrometry) confirmed the presence of the formic acid (Figure S9).

Another isotope labelling experiment gave us an indirect evidence about an intermediate species generated during the reaction. The ^{18}O-labled CO_2 was used to follow the reaction between the W=^{16}O and $C^{18}O_2$. The reaction was stopped after 2 days (as opposed to 4 days) and the reaction mixture was examined by IR spectroscopy. The isotopic shift of the formate-carbonyl (1640 ⟶ 1603 cm^{-1}) was observed from the reaction between $C^{18}O_2$ and complex **1** as expected. At this time, due to the incomplete reaction resulted from a shorter reaction time, an interesting insight was gained. We observed that both of the W=O peaks of the complexes **1** and **2** were shifted, as complex **1**: 895 → 848 cm^{-1} and complex **2**: 918 → 871 cm^{-1} (Figure 4d). This indicates that W=^{16}O of **1** exchanges its oxygen atom with those from $C^{18}O_2$ possibly through a W-carbonate intermediate. This is a similar reactivity pattern to that of our previously reported system[26] and reminiscent of the computational study of the enzyme W-FDH active site which suggests the formation of a W-thiocarbonate intermediate.[27]

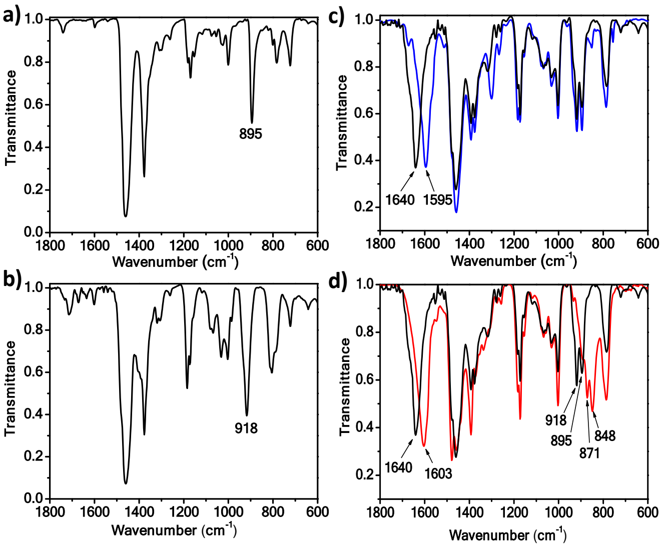


Figure 4. IR spectra (Nujol) of a) $[W^{IV}O(S_2C_2Me_2)_2](NEt_4)_2$ (**1**), b) $[W^V_2O_2(\mu\text{-}S)(\mu\text{-}S_2C_2Me_2)(S_2C_2Me_2)_2](NEt_4)_2$ (**2**), c) the products mixture from the reaction of **1** at 90 °C for 2 days under $^{12}CO_2$ (black solid line) and $^{13}CO_2$ (blue solid line), and d) the products mixture from the reaction of **1** at 90 °C for 2 days under $C^{16}O_2$ (black solid line) and $C^{18}O_2$ (red solid line).

In the generation of formate from the reaction of **1**/CO_2, a proton source is necessary. Although we cannot completely rule out the acetonitrile solvent as a proton source, we suspected that a trace amount of water in solvent would be a source for the proton because there is no strong base in the reaction mixture. Therefore, we re-examined the reaction by adding water (5 %) into the reaction in acetonitrile. The reaction, however, did not result in the formate nor complex **2**. Rather, it yielded a green decomposed species - fully oxidized inorganic W-oxides, consistent with the known proton/moisture sensitivity of W^{IV}=O species.[34] This result suggests that the proton delivery into the catalytic site must be in a controlled manner for an efficient conversion of CO_2 to formate. Indeed, the W-FDHs have the highly conserved amino acid residues (SeCys^{140}-CH_2-Se-H) in the secondary coordination sphere of the CO_2 binding site that can regulate the supply of protons to the (thio)carbonate intermediate in a sophisticated manner.[27] Another important difference between the enzyme active site and the current synthetic model is an incomplete structural mimic of pyranopterin-dithiolate ligand, MPT (Figure 1). The ligand used in our model compound concerns only about the dithiolene moiety, the primary coordination environment. However, the MPT ligand found in the enzyme is a dithiolene that is fused with the redox-active pterin moiety, which can play an important role in the enzyme catalysis.[35, 36] It is conceivable that the presence of the pterin moiety in the ligand periphery might prevent the unwanted bond cleavage of the ligand observed in our model compound. Indeed, a recently reported Ni bis(dithiolene) electrocatalyst capable of converting CO_2 to formate employs an MPT analogue, in which opening of the pyran ring of the ligand is a critical feature to achieve the catalytic activity.[37]

In summary, we have demonstrated a novel CO_2 reactivity of the bis-dithiolene W^{IV}=O complex, a biomimetic complex for the active site of the W-dependent formate dehydrogenase (W-FDH). The reported bis-dithiolene W^{IV}=O complex reduces gaseous CO_2 to formate at 90 °C, while the W^{IV}=O becomes oxidized by CO_2 to form an unprecedented triply bridged dinuclear W^{V}=O dithiolene complex. These results provide insights into the importance of the secondary coordination environment and the synthetic strategies for the biomimetic CO_2 reduction catalysts. The features of the biomimetic FDH catalysts in the next generation would include a proton delivery moiety and a dithiolene appended by the pterin moieties in the ligand.

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Conflicts of interest

There are no conflicts of interest to declare.

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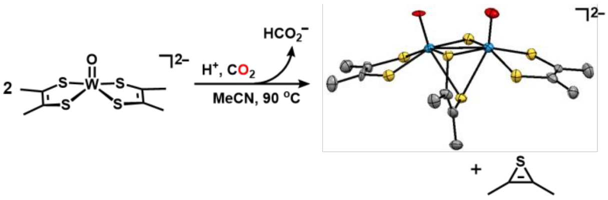

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