



Hydrogen generation: Aromatic dithiolate-bridged metal carbonyl complexes as hydrogenase catalytic site models



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ABSTRACT

The design, syntheses and characteristics of metal carbonyl complexes with aromatic dithiolate linkers reported as bioinspired hydrogenase catalytic site models are described and reviewed. Among these the complexes capable of hydrogen generation have been discussed in detail. Comparisons have been made with carbonyl complexes having alkyl dithiolates as linkers between metal centers.

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1. Introduction

The global energy consumption is on the rise with every passing day. Hence, the growing interest in the development of catalysts for hydrogen which is considered as the future energy carrier. The ideal catalyst for this purpose is platinum which is however, expensive and may not be sustainable for a large scale hydrogen economy. In nature, three types of hydrogenase (H_2ase) enzymes: [Fe], [FeFe] and [NiFe] catalyze the formation and oxidation of hydrogen [1–4]. Out of these three vital enzymes, [FeFe] H_2ases isolated from *Desulfovibrio desulfuricans* and *Clostridium pasteurianum* are the most efficient catalysts that generate hydrogen at low overpotentials and at very high turnover frequencies (TOFs), i.e. 6000–9000 s^{-1} [5–11]. Crystallographic characterization of the enzyme has revealed that the active site consists of two iron centers (proximal, Fe_p and distal, Fe_d) with a bridging dithiolate ligand [2,3]. In addition CO, CN^- (CO = carbonyl; CN^- = cyanide) ligands and a cysteine-linked [4Fe4S] cluster complete the coordination sphere [12–18]. In an effort to model the enzyme active site and design efficient catalysts, a large number of complexes with altering bridging dithiolate ligands (both alkyl and aromatic) and a combination of CO and σ -donating ligands have been reported so far [1,19–38].

Though there are many reviews discussing the synthetic models of the [FeFe] H_2ases in general, there is none that focuses on aromatic dithiolate-bridged iron carbonyl complexes as catalysts for hydrogen generation. Therefore, this review will focus on aromatic dithiolate bridged mono-, di- and polynuclear iron carbonyl complexes that

have been reported to date (Figs. 1–9) [39–98]. A few complexes reported with other metals i.e. Ru [89–91], Os [91], Mn [61,92] and Co [97,98] will also be discussed. The characteristics and catalytic properties of such complexes will be discussed with respect to the complexes with $-S-CH_2XCH_2-S-$ linkage (X = O, S, CH_2 , NH). Even though the aromatic dithiolate(dt)-bridged complexes do not resemble the enzyme active site in structure, the importance lies in the fact that the aromatic dithiolate-bridged complexes lead to more stable reduction products and isolable hydride intermediates in comparison to the aliphatic complexes. The reduction products and hydride intermediates generated during the proton reduction cycle will be discussed. The study of aromatic dithiolate-bridged carbonyl complexes is also interesting because due to their robustness (rigid and unsaturated nature of the bridging ligand) they could be promising catalysts for photochemical hydrogen evolution as has been demonstrated by Ott [76] and Wasielewski [60]. Based on the aromatic dt bridge, the complexes discussed in the review have been classified into three categories: (i) complexes with aromatic dt ligands other than benzenedithiolate (bdt) [43–60]; (ii) complexes with substituted bdt ligands [58–72] and (iii) complexes with bdt ligand [73–90]. In addition, polynuclear and mononuclear iron complexes have also been discussed. The FTIR and electrochemical data for all the reported complexes are summarized in Tables 1–3.

2. Bioinspired hydrogenase active site model complexes

2.1. Polynuclear iron–sulfur complexes

Though a large number of complexes with alkyl dithiolate bridges ($-S-CH_2CH_2CH_2-S-$; $-S-CH_2OCH_2-S-$; $-S-CH_2N(CH_2CH_2CH_3)$

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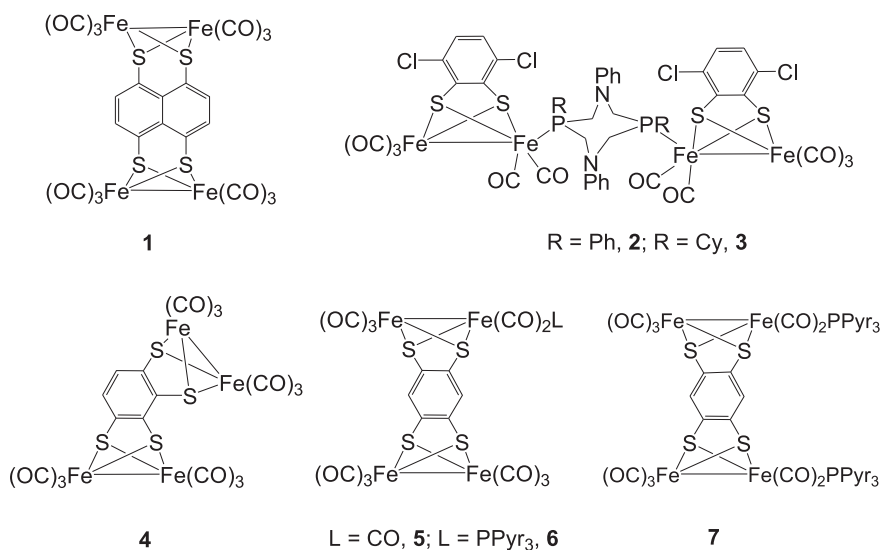


Fig. 1. Tetranuclear iron–sulfur carbonyl complexes.

$\text{CH}_2\text{-S-}$; $-\text{S-CH}_2\text{CH}(\text{OCH}_2\text{Ph})\text{CH}_2\text{-S-}$; $\text{MeSi}(\text{CH}_2\text{S-})_3$) have been reported [99–105] there are not many examples known of the tetranuclear iron carbonyl complexes (1–7) with aromatic dithiolate bridges [39–42] (Fig. 1). A rare example of a complex (8) of higher nuclearity is also known (Fig. 2) [42]. The tetranuclear iron carbonyl complex $(\mu\mu\text{-ttn})[\text{Fe}_2(\text{CO})_6]_2$ **1** (ttn = tetrathionaphthalene) was first reported by Parthasarathy and coworkers in 1977 (Fig. 1) [39]. It was synthesized by treating $\text{Fe}_2(\text{CO})_9$ with ttn. This complex was reported as a new class of organometallic compounds.

Tetranuclear complexes $[(\mu\text{-Cl}_2\text{bdt})\text{Fe}_2(\text{CO})_5]_2(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)]$ **2** and $[(\mu\text{-Cl}_2\text{bdt})\text{Fe}_2(\text{CO})_5]_2(\text{P}^{\text{Cy}}_2\text{N}^{\text{Ph}}_2)]$ **3** (Cl_2bdt = 1,4-dichlorobenzene-1,2,3,4-tetrathiolato; $\text{P}^{\text{R}}_2\text{N}^{\text{Ph}}_2$ = 1,5-diaza-3,7-diphospha-cyclooctane ligands, R = phenyl, Ph or cyclo-hexyl, Cyc) reported by Ott and co-workers are examples in which the cyclic phosphine ligand (P_2N_2) acts as a bridge between the iron centers (Fig. 1) [40]. Though a large number of catalytically active mono and dinuclear complexes of P_2N_2 ligands are known [5,94,106–108], the tetranuclear complexes **2** and **3** have not been tested for any catalytic activity. The ν_{CO} frequencies are in the range of terminal carbonyls and higher in energy than the propanedithiolate (pdt), substituted-pdt, oxadithiolate (odt) or azadithiolate (adt) ligands (Table 1) [103–106,109]. The stability of complex **2** was improved in comparison to **3** due to phenyl substitution at the phosphorus atoms.

The other reported tetra-iron carbonyl complexes are $(\mu\mu\text{-obtt})[\text{Fe}_2(\text{CO})_6]_2$ **4**; $(\mu\mu\text{-pbtt})[\text{Fe}_2(\text{CO})_6]_2$ **5**; $(\mu\mu\text{-pbtt})[\text{Fe}_2(\text{CO})_6][\text{Fe}_2(\text{CO})_5$

(PPyR_3)] **6** and $(\mu\mu\text{-pbtt})[\text{Fe}_2(\text{CO})_5(\text{PPyR}_3)]_2$ **7** (obtt = benzene-1,2,3,4-tetrathiolato; Ppyr = N-pyrrolyl and pbtt = benzene-1,2,4,5-tetrathiolato) (Fig. 1) [41]. Complexes **4** and **5** [42] displayed four-electron reduction processes (two two-electron reversible reduction events) in their electrochemistry which was also confirmed by bulk electrolysis experiments. The reduction potentials are less negative than those of the $[\text{FeFe}]$ complexes, $(\mu\text{-pdt})[\text{Fe}_2(\text{CO})_6]$ **A** (irreversible one-electron reductions at -1.74 and -2.35 V vs. Fc/Fc^+ in dichloromethane) (Fc/Fc^+ = ferrocene/ferrocenium) [110] and $(\mu\text{-bdt})[\text{Fe}_2(\text{CO})_6]$ (reversible two-electron reduction at -1.44 vs. Fc/Fc^+ in dichloromethane) [62]. The difference between the first and second reduction potentials ($\Delta E = E_{1/2}^{\text{red}1} - E_{1/2}^{\text{red}2}$) for **4** and **5** was found to be 270 and 280 mV, respectively. This difference of 270 and 280 mV has been attributed to the electronic communication between the iron atoms of the Fe_2S_2 units through the benzene ring of the tetrathiolato ligand. In contrast, complexes **6** and **7** displayed slightly reversible consecutive two-electron reduction events (Table 2). The cathodic shift of the reduction potentials in **6** and **7** is small in comparison to the all carbonyl complex **5**. This is probably due to the weak electron donating character of the phosphine ligand, PPyR_3 as compared to other complexes reported with trialkylphosphines and triphenylphosphine, PPh_3 [111–113]. Complexes **4–7** were tested for proton reduction by using a range of organic acids (CH_3COOH , CH_2ClCOOH , CHCl_2COOH , CCl_3COOH and CF_3COOH). Complex **5** displayed a new reduction wave at $E_p^{\text{red}} = -1.57$ V, the current height of which did not increase on addition of excess acid. In addition two oxidation waves were observed at -0.51 V and -0.66 V. Similar behavior was also observed for complex **4**. As verified by DFT (density functional theory) calculations and ^1H NMR (signals at δ 7.40, δ 6.89 for the benzene ring protons and at δ -8.79 for the hydride), the reduced and protonated form 5H^- was reported to contain a bridging hydride with an unsymmetric structure that resulted from the cleavage of one of the Fe–S bonds as also reported for complex **92** discussed later on (Fig. 3). On the other hand, for **5** only one signal at δ 6.98 is observed for the benzene ring, which is probably because **5** is more symmetric than 5H^- . Tilley and co-workers have also suggested similar chemical shift values for the bridging hydride species of complex $(\mu\text{-bdt})[\text{Fe}_2(\text{CO})_6]$ (δ -8.79) (Fig. 3) [83].

Complexes **4–7** are not catalytically active in the presence of acetic acid as was also the case with the bdt complex $(\mu\text{-bdt})[\text{Fe}_2(\text{CO})_6]$ [59, 73,74]. The catalytic cycle for complex **5** was suggested to proceed via two ECC (E = electrochemical; C = chemical) cycles (Scheme 1). The first one is proposed with stronger acids, CCl_3COOH , CF_3COOH and the second cycle is proposed with weaker acids, CH_2ClCOOH , CHCl_2COOH .

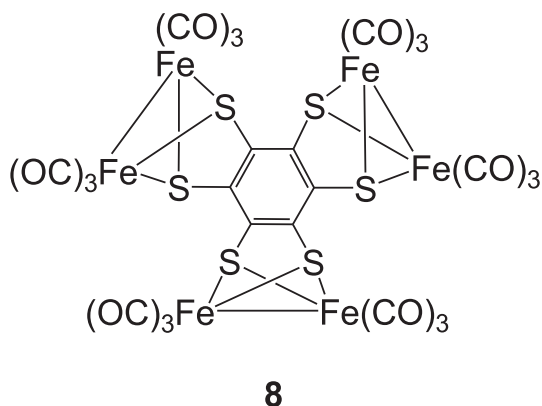


Fig. 2. Hexanuclear iron–sulfur cluster complex.

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