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A DFT study of structure and electrochemical properties of diiron-hydrogenase models with benzenedithiolato and benzenediselenato ligands†

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The diiron benzenedithiolato carbonyl complex is a biomimetic catalyst for proton reduction whose catalytic pathways depend on the solvent properties and the proton donor acidity. Previous studies showed that the initial steps in electrocatalytic generation of dihydrogen in acetonitrile involve a two-electron reduction followed by protonation, but the structures and physical properties of other intermediates are not known. We have performed a systematic quantum chemical analysis of the reduced and protonated complexes with benzenedithiolato and benzenediselenato ligands that can be formed by addition of up to three electrons and/or protons. The exchange of the sulfur atoms by selenium increases the basicity of the iron atoms but is not favorable for the protonation of the chalcogen atoms. Our results show that the most stable singly protonated complexes possess the proton in a bridging position between both irons, irrespective of the total complex charge. The second proton can be attached to a chalcogen atom or to an iron atom in a terminal position, depending on the complex charge. The most stable isomers of the triply protonated complexes have protons in the bridging and terminal positions as well as one proton bound to a chalcogen atom. Standard reduction potentials and acidities of all examined complexes were computed. We also discussed possible intermediates and reaction pathways in the electrocatalytic proton reduction to molecular hydrogen formation.

1 Introduction

The transformation of electrical energy into chemical energy by electrochemical reduction of protons to form molecular hydrogen has gained considerable attention as a promising process for the global aim to switch to a clean fuel economy.¹ Although H₂ formation is efficiently catalysed by noble metals, cheaper catalysts based on abundant materials are desirable for broad application. Viable alternatives to the currently used noble metal catalysts for large-scale electrochemical production of H₂ are complexes based on the first d-block transition metals.²

Particularly promising are biomimetic catalysts^{3–12} inspired by the Fe₂S₂ active site of iron–iron hydrogenases, a class of enzymes responsible for dihydrogen production in microbes.^{13,14} For example, a diiron complex containing a benzenedithiolato (bdt) ligand and six carbonyl groups (*i.e.* Fe₂(bdt)(CO)₆, see Fig. 1) was shown to be a robust proton reduction catalyst.^{15–27} The conjugated bdt ligand modulates the electronic properties of the iron atoms in such a way that the catalyst exhibits mild reduction potentials and a solvent-dependent reduction potential inversion.^{17,18} The latter implies that in acetonitrile and dichloromethane, it is easier to reduce the anionic complex, M[−], than the neutral complex, M, so that in practice always a two-electron reduction takes place. In acetonitrile, the reduction potentials for M and M[−] are E₁ ≈ −1.3 V and E₂ ≈ −1.15 V versus the ferrocene electrode, respectively.^{17,18} Instead, no potential inversion is

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† Electronic supplementary information (ESI) available: The standard reduction potentials computed with different density functionals, relative electronic energies of states with different multiplicities, and optimized isomers of the singly, doubly and triply protonated complexes with the benzenedithiolato ligand and their relative free energies. See DOI: 10.1039/c9nj04887a

Fig. 1 Chemical structure of the Fe₂(bdt)(CO)₆ complex.

observed in THF solvent ($E_1 = -1.485$ V, $E_2 = -1.500$ V), which has been attributed to a larger donor number of THF compared to that of acetonitrile.¹⁸

Reduction of the complex makes it more basic and thus more prone to protonation, which is a crucial step in the dihydrogen formation. Capon *et al.*¹⁷ found that both weak ($pK_a \sim 23$) and strong ($pK_a \sim 8$) acids in acetonitrile solution stimulate formation of a stable MH^- complex, which led them to conclude that the pK_a of the MH^- anion is larger than 23. Based on this observation, the authors proposed that the protonation of M^- is not competitive with its reduction. Furthermore, they proposed that the rate determining step in the reduction of protons from strong acids is the protonation of MH^- . In addition, a stable doubly protonated complex was not observed. Felton *et al.*, using more negative potentials than Capon *et al.*, observed the reduction of protons from weak acids at approximately -2.1 V *versus* the ferrocene electrode in acetonitrile.¹⁸ They argued that weak acids are not able to protonate MH^- , but that instead this intermediate first has to be further reduced to MH^{2-} before subsequent second protonation can occur. The authors postulated that the rate determining step in the case of weak acids is the protonation of the M^{2-} anion. In addition, they proposed that dihydrogen formation is a fast process in which MH^{2-} reacts directly with an acid. Interestingly, no catalysis was noticed with acids weaker than $pK_a = 25.5$. Felton *et al.* argued that the actual catalyst is the M^- anion and that the catalysis proceeds with an ECEC mechanism (E stands for electron transfer, C stands for chemical reaction).

Quantum chemical calculations by Felton *et al.* revealed that the protonation of M^{2-} occurs at the bridging position in between the two iron atoms in the complex. This binding site was also argued to be important for protonation of the M^- anion created in photoinduced one-electron processes.²³ Mirmohades *et al.* estimated that the pK_a of MH in acetonitrile is less than 12.7.²³ Based on NMR spectroscopy and quantum chemical calculations, Wright *et al.*¹⁹ concluded that in addition to the bridging MH^- hydride, the terminal isomer is also present to a minor extent in THF solvent. Liu *et al.*²⁴ performed an extensive experimental and theoretical study of intermediate species. In the presence of excess strong acid, the authors observed a triply protonated complex, which they attributed to an intermediate complex involved in the proton reduction catalysis.

The catalytic properties of the biomimetic catalyst could be improved by structural modification of the bridgehead group. Gao *et al.* showed that exchange of the bdt ligand by a pyrazinedithiolato ligand positively shifted the reduction potential of the complex by approximately 0.2 V.^{5,10} This is a consequence of electron density decrease at the iron atoms due to electron-withdrawing inductive interaction with the electronegative nitrogen atoms. The catalysis was observed at -2.21 V, which is 0.11 V more negative than in the case of the bdt ligand. On the other hand, substitution of the sulfur atoms in the Fe_2S_2 core by selenium might increase the basicity of the iron atoms since this change is expected to increase the electron density at the diiron core. Selenium and sulfur belong to the same group in the periodic table, hence the structures of the intermediates

in the proton reduction cycle should not differ significantly upon substitution. Previously, sulfur/selenium substitution at the bridging dithiolate ligands has been examined for several biomimetic models,^{28–32} but a detailed investigation of the substitution effects on all reaction intermediates of the $Fe_2(bdt)(CO)_6$ catalyst is still lacking.

Here, we perform a theoretical study of the proton reduction pathways catalyzed by the $Fe_2(bdt)(CO)_6$ complex, in which we systematically characterize all possible intermediate species that can be formed by reduction and/or protonation of up to three electrons/protons. Included in our analysis are not only the lowest energy structures, but also the different tautomers that can exist for each species related to the different protonation sites. In addition to the bdt ligand, we also examine the complex with the benzenediselenato (bds) ligand, which is formed by the sulfur/selenium substitution in the bdt ligand. The paper is organized as follows. In the next section, we summarize the computational details of our calculation methodology. In the subsequent sections, we present our results of the most stable isomers in their different oxidation states, starting from the unprotonated complexes up to the triply protonated complexes. We compute infrared spectra of these structures to compare with experimental results. We also discuss the standard reduction potentials and the acidities of the examined complexes. The paper ends with our concluding remarks.

2 Computational details

All calculations were performed with the TURBOMOLE program package.³³ We employed density functional theory (DFT) with the resolution-of-identity (RI) approximation³⁴ and the TPSSh³⁵ functional for geometry optimizations and electronic energy calculations. The TPSSh functional is a hybrid version of the TPSS³⁶ functional, which is based on a nonempirical meta-generalized gradient approximation. In a recent benchmark study, it has been shown that the TPSSh functional is particularly suitable for transition metals and bioinorganic compounds.³⁷ All electrons were correlated in the calculations. Molecular structures were optimized with the def2-SVP basis set.³⁸ The triple- ζ plus polarization and diffuse functions basis set (def2-TZVPD) was used to compute electronic energies at these geometries. All analyzed complexes have a low-spin ground state. Benchmarking of several other density functionals on reduction potentials and relative energies of different spin states is provided in the ESI† The conductor-like screening model (COSMO) implemented in TURBOMOLE^{39,40} was utilized in the present work to study the complex in acetonitrile. In order to account for solvent effects on the geometries, all structures were optimized in acetonitrile. The calculated frequencies were scaled with the scaling factor 0.97. Free energies were computed employing the direct approach⁴¹ which avoids separate computation of gas phase and solvation free energies. The vibrational-rotational contribution to the free energies was approximated by the harmonic-rigid-rotor approximation. In cases where the spin multiplicity was doublet, the contribution due to electronic spin degeneracy was included in the free energy calculations.

All potentials in acetonitrile were calculated relative to the ferrocene electrode. The absolute redox potential of the Fe^+/Fe couple was computed to be 4.56 V within the employed computational model. The solvation energy of a proton in acetonitrile ($-1088.68 \text{ kJ mol}^{-1}$) was taken from the study by Riplinger and Carter.⁴² Partial atomic charges were computed employing the natural population analysis⁴³ implemented in TURBOMOLE.

3 Results and discussion

In the present work, the chalcogen atoms (*i.e.* S or Se) are labeled X. We examined three proton binding sites: the proton can be attached to a Fe atom in a terminal (t) position, to both Fe atoms in a bridging (b) position or to a chalcogen atom (x). The geometrical distortions created by the exchange of sulfur by selenium atoms are relatively small and therefore we show in figures only one structure representing both bdt and bds ligands. Of course, these small structural changes are still indicative for the modification of the electron density upon the ligand exchange. Another descriptor of the charge distribution⁴⁴ is provided by analysis of the partial atomic charges. Although the actual values of such charges are fractional and depend on the employed partition scheme, they provide valuable insight into the change of iron basicity upon reduction and upon chalcogen atom substitution. We will also discuss the carbonyl stretching frequencies since these are sensitive to changes in the electronic density and have high intensities, which makes them a good probe for spectroscopic measurements^{23,24,45}

3.1 Unprotonated complexes

The optimized geometries of the neutral, singly, doubly and triply reduced complexes are shown in Fig. 2, and several selected bond lengths of these structures are collected in Table 1. The neutral complex belongs to the C_{2v} symmetry point group. The calculated bond lengths of the complex with the bdt ligand are in very good agreement with the ones obtained by X-ray diffraction.⁴⁶ The distance between the two Fe atoms in the oxidized state amounts to 2.45 Å, which is 0.03 Å shorter than the experimental value.⁴⁶ Previous computational studies using the VWN/TZP¹⁸ and BP86/def2-TZVP²⁴ levels of theory reported Fe–Fe bond lengths of 2.47 and 2.52 Å, respectively. Thus, the employed meta-hybrid functional provides

Table 1 Selected bond lengths (in Å) in the unprotonated complexes in the different oxidation states and with the different bdt and bds bridging ligands. The parenthesized numbers are experimental distances obtained from X-ray diffraction experiments

Bond	M		M^-		M^{2-}		M^{3-}	
	bdt	bds	bdt	bds	bdt	bds	bdt	bds
$\text{Fe}_1\text{--Fe}_2$	2.45 (2.48) ^a	2.40	2.50	2.52	2.54 (2.53) ^b	2.56	2.60	2.60
$\text{Fe}_1\text{--X}_1$	2.30 (2.27) ^a	2.49	2.29	2.39	2.35 (2.32) ^b	2.44	2.37	2.47
$\text{Fe}_1\text{--X}_2$	2.30 (2.27) ^a	2.49	3.05	3.09	3.74	3.86	3.68	3.79
$\text{Fe}_2\text{--X}_1$	2.30 (2.27) ^a	2.49	2.29	2.39	2.28 (2.24) ^b	2.38	2.71	2.84
$\text{Fe}_2\text{--X}_2$	2.30 (2.26) ^a	2.49	2.35	2.45	2.35 (2.34) ^b	2.46	2.38	2.48

^a Ref. 46. ^b Dimeric sodium derivative of M^{2-} , ref. 19.

a shorter Fe–Fe bond than the functionals based solely on the local density or the generalized gradient approximation. The computed Fe–S bond lengths are found to be 2.30 Å, which is 0.03 Å longer than the experimental values. The VWN¹⁸ and BP86²⁴ functionals provided almost the same value of these bonds as the current TPSSH functional. The substitution of sulfur by selenium leads to a decrease of the Fe–Fe bond length by 0.05 Å and an elongation of the iron–chalcogen bond by 0.19 Å.

The singly reduced complex is characterized by the breaking of an iron–chalcogen bond. In the complex with the bdt ligand, the $\text{Fe}_1\text{--Fe}_2$ and $\text{Fe}_2\text{--S}_2$ bonds are elongated by 0.05 Å relative to the neutral complex. On the other hand, the $\text{Fe}_1\text{--S}_1$ and $\text{Fe}_2\text{--S}_1$ bonds remain almost unaltered. The exchange of sulfur by selenium elongates the Fe–Fe distance by 0.02 Å. Larger changes are found for the iron–chalcogen bond lengths. The doubly reduced complex exhibits further elongation of the $\text{Fe}_1\text{--Fe}_2$ and $\text{Fe}_1\text{--X}_2$ bonds. Also, one carbonyl group is placed in the bridging position. The computed bond lengths of the doubly reduced complex with the bdt ligand are also in a very good agreement with the values from X-ray diffraction.¹⁹ The geometry of the triply reduced complex is similar to that of the doubly reduced complex, although the bond lengths are somewhat longer. The exception is the $\text{Fe}_1\text{--X}_2$ distance, which is shorter by 0.06 and 0.07 Å for the bdt and bts ligands, respectively. The $\text{Fe}_1\text{--Fe}_2$ distance amounts to 2.60 Å for both ligands.

Table 2 shows the partial atomic charges of the iron atoms and the sulfur or selenium atoms in the different oxidation states of the unprotonated complex. The exchange of sulfur by selenium in the neutral complex leads to an increase of electron density on the iron atoms and a decrease on the chalcogen

Fig. 2 Optimized geometries of the unprotonated complexes in the different oxidation states.

Table 2 Partial atomic charges (in atomic units) for selected atoms of the unprotonated complexes in the different oxidation states and with the different bdt and bds bridging ligands

Atom	M		M [−]		M ^{2−}		M ^{3−}	
	bdt	bds	bdt	bds	bdt	bds	bdt	bds
Fe ₁	−0.43	−0.48	−0.23	−0.28	−0.37	−0.41	−0.24	−0.26
Fe ₂	−0.43	−0.48	−0.46	−0.50	−0.50	−0.52	−0.47	−0.49
X ₁	0.12	0.27	0.05	0.18	−0.25	−0.22	−0.33	−0.31
X ₂	0.12	0.27	−0.12	−0.03	0.05	0.17	−0.19	−0.13

atoms. Reduction of this complex results in accumulation of positive charge on the Fe₁ and of negative charge on the chalcogen atoms. The changes in the latter are larger for the X₂ atom, which explains the elongation of the Fe–X₂ bonds. The second reduction mostly increases the electron density at the Fe₁ and X₁ atoms, whereas it decreases at the X₂ atom. In the triply reduced complexes, the iron atoms are more positive and the chalcogen atoms are more negative compared to the doubly reduced complex. Note that the differences in the iron charges between the triply reduced complexes with the bdt and the bds ligands are very small.

Fig. 3 shows the computed infrared spectra of the CO stretching modes of the complexes in the different oxidation states in acetonitrile solvent together with experimental spectra²³ (bdt ligand only) in the same solvent. The discrepancies between the computed and the experimental spectra partly results from the chosen electronic structure method and basis set, but more importantly, from neglecting anharmonic effects. Nevertheless, there is overall a good agreement between the computed and experimental spectra. The experimental peaks of the neutral complex appear at 2004, 2044 and 2080 cm^{−1}. The computed spectrum consists of the six CO bands, in which the lowest two have negligible intensities. The two high frequency experimental

peaks are well reproduced by the computed peaks at 2042 and 2083 cm^{−1}. The low-frequency experimental peak at 2004 cm^{−1} is broader than the other two peaks. Our results indicate that it consists of two closely spaced bands, which are computed to be at 2013 and 2015 cm^{−1}.

Reduction of the complex shifts the CO bands to lower frequencies. The experimental spectrum of the singly reduced complex consists of three peaks at 1890, 1980 and 2035 cm^{−1}, respectively.²³ As in the case of the neutral complex, we nicely reproduce the two high frequency peaks. Moreover, we can assign the shoulder of the peak at 1980 cm^{−1} to two medium intensity transitions. Our computed value of the lowest frequency C=O mode is blue-shifted relative to the experimental value by approximately 30 cm^{−1}.

The experimental infrared spectrum of the doubly reduced complex (shown in panel c) exhibits four distinct peaks at 1682, 1865, 1914 and 1964 cm^{−1}.²³ We assign the peak at 1682 cm^{−1} to the CO stretching mode of the bridging carbonyl group. Our calculated frequency of this mode is 50 cm^{−1} blue-shifted relative to the experimental value. The broad experimental peak at 1865 cm^{−1} comes from three CO modes that are computed to be at 1877, 1892, and 1898 cm^{−1}. The intensities and positions of the two highest frequency experimental peaks are well-reproduced in our calculations. The vibrational spectral density of the triply reduced complex resembles the one of the doubly reduced complex.

Substitution of the sulfur atoms by selenium has only very small effects on the spectra of the neutral, singly and doubly reduced complexes. On the triply reduced complex, the effect of the substitution is larger. In particular, all transitions are red-shifted upon S/Se exchange but their intensities remain essentially the same. It is encouraging that the selected computational method very-well reproduces the infrared spectra of the CO stretch vibrations. In the next sections, we will predict infrared spectra for complexes for which no experimental spectra are yet available.

3.2 Singly protonated complexes

The optimized geometries of the most stable isomers of the singly protonated complexes in different oxidation states are presented in Fig. 4. Our results show that the lowest-energy isomer has the proton in the bridging position regardless of the oxidation state. The free energy difference between the bridging hydride isomer and the terminal hydride one becomes smaller after each reduction (it will become clear hereafter from the charge analysis that the proton has become a hydride upon binding to iron). We find that the terminal hydride isomer of the complex with the bdt ligand is only 4 kJ mol^{−1} less stable than the bridging one when the complex has reached a total charge of −2. The isomers in which the proton has binded to a chalcogen atom are significantly less stable than the bridging isomers, irrespective of the total charge (the relative isomer energies are given in the ESI†).

Table 3 lists several selected bond lengths of the singly protonated complexes compared to experimental estimates. Let us first compare the computed bond lengths of the MH(b)⁺

Fig. 3 Computed infrared spectra of the unprotonated complexes in acetonitrile solvent in the different oxidation states: M (panel a), M[−] (b), M^{2−} (c), and M^{3−} (d), and the different bridging bdt (black stick lines) and bds (red stick lines) ligands. Black dashed lines show digitalized experimental infrared spectra²³ of the CO stretching bands of the complexes with the bdt ligand.

Fig. 4 Optimized geometries of the most stable isomers of singly protonated complexes.

Table 3 Selected computed and experimental (in parentheses) bond lengths (in Å) of the singly protonated complexes. The experimental distances are obtained from X-ray diffraction experiments²⁴

Bond	MH(b)+		MH(b)		MH(b) [−]		MH(b) ^{2−}	
	bdt	bds	bdt	bds	bdt	bds	bdt	bds
Fe ₁ –Fe ₂	2.54 (2.54)	2.58	2.62	2.75	2.55	2.56	2.62	2.63
Fe ₁ –X ₁	2.31 (2.27)	2.41	2.30	2.46	2.35	2.44	2.38	2.48
Fe ₁ –X ₂	2.31 (2.27)	2.41	2.78	2.46	3.93	4.06	3.91	4.05
Fe ₂ –X ₁	2.31 (2.27)	2.41	2.30	2.46	2.29	2.39	2.67	2.80
Fe ₂ –X ₂	2.31 (2.27)	2.41	2.34	2.46	2.36	2.47	2.39	2.50
Fe ₁ –H	1.66 (1.63)	1.66	1.68	1.68	1.62	1.63	1.61	1.62
Fe ₂ –H	1.66 (1.66)	1.66	1.65	1.68	1.74	1.73	1.77	1.75

isomer with those from X-ray diffraction.²⁴ We find a very good agreement between the computed and experimental bond lengths. The Fe₁–Fe₂ distance is 2.54 Å in both cases. The average experimental Fe–S bond length is 2.27 Å,²⁴ which is 0.04 Å shorter than our value. The computed Fe₁–H and Fe₂–H bond lengths (1.66 Å) are equal, whereas there is a slight asymmetry in the experimental structure (1.66 and 1.63 Å). Upon reduction, the Fe₁–Fe₂ bond length of the complexes with the bdt ligand fluctuates in the range from 2.54 to 2.62 Å.

The asymmetry in the Fe₁–H and Fe₂–H bond lengths, seen experimentally in the most-oxidized complex, MH(b)⁺, becomes more pronounced with every further reduction of the protonated complex. In the singly, doubly and triply reduced complexes, the difference between these bond lengths amounts to 0.03, 0.12, and 0.16 Å, respectively. Note also that a carbonyl group is transferred into a bridging position for the doubly and triply reduced complexes. Substitution of the sulfur atoms by selenium results in longer Fe–Fe and Fe–X bonds. In addition, there is a difference in symmetries of the MH(b) complexes with the bdt and bds ligands: in the case of the bdt ligand the Fe₁–S₂ bond is broken, whereas in the case of the bds ligand the structure has C_{2v} symmetry.

Selected partial atomic charges of the singly protonated complexes are collected in Table 4. The charge of the bridging hydrogen atom is very small or negative irrespective of the total charge of the complex, implying that there is considerable electron density on this atom. Only the charge of the X₂ atom exhibits a clear trend with respect to subsequent reductions – its value decreases.

Having discussed the structures and stability of the single protonated complexes, let us turn to the infrared spectra of the

Table 4 Partial atomic charges (in atomic units) for selected atoms of the singly protonated complexes in the different oxidation states

Atom	MH ⁺		MH		MH [−]		MH ^{2−}	
	bdt	bds	bdt	bds	bdt	bds	bdt	bds
Fe ₁	−0.49	−0.55	−0.34	−0.51	−0.60	−0.61	−0.58	−0.60
Fe ₂	−0.49	−0.55	−0.52	−0.51	−0.48	−0.52	−0.34	−0.37
X ₁	0.21	0.38	0.14	0.22	0.13	0.27	−0.09	0.00
X ₂	0.21	0.38	−0.01	0.22	−0.20	−0.14	−0.27	−0.23
H	0.00	−0.01	−0.05	−0.02	0.01	0.00	−0.02	−0.03

CO stretching bands of these structures. Comparison of the computed and experimental spectra may reveal which isomers are present under experimental conditions. The computed and digitalized experimental spectra in dichloromethane solution²⁴ are presented in Fig. 5. In all cases, we have plotted the computed infrared spectrum of the most stable bridging isomer. The computed spectra of the MH⁺(b) and MH(b) isomers nicely matches the experimental ones. However, the peaks around 1650 cm^{−1} likely originate from a carbonyl group in a bridging position. Thus, we propose that the bridging isomers with a carbonyl group in the bridging position are also

Fig. 5 Computed infrared spectra of singly protonated complexes with the bdt (black stick lines) and bds (red stick lines) ligands and digitalized experimental²⁴ infrared spectra of the CO stretching bands of singly protonated complexes with the bdt ligand: (a) MH(b)⁺, (b) MH(b), (c) MH(b)[−], and (d) MH(b)^{2−}. The computed and experimental spectra are in acetonitrile and dichloromethane, respectively.

present in dichloromethane solution. The computed spectrum of $\text{MH}^-(\text{b})$ reproduces the experimental intensity distribution, but the peak positions are blue-shifted. This implies a large anharmonic coupling among the CO stretching modes in the $\text{MH}^-(\text{s})$ complex. The computed spectrum of the $\text{MH}^{2-}(\text{b})$ isomer has transitions that appear at even lower frequencies than in other singly protonated complexes. Its maximum intensity was computed to be at 1914 cm^{-1} . It is interesting to note that a mode related to the hydride motion in the bridging hydride isomers appears between 1400 and 1500 cm^{-1} (data not shown) with a strong intensity. This mode is therefore a useful signal for the assignment of bridging hydride isomers.

3.3 Doubly protonated complexes

Doubly protonated complexes are formed by protonation of the singly protonated complexes. Here, we consider the following cases: (b,t), (t,x), and (x,b). We also examine (t,t) isomers, in which two protons are either bound to the same iron atom, forming a dihydrogen complex, (t_1, t_1) , or to different iron atoms, (t_1, t_2) , forming a dihydride complex. The optimized geometries of the most stable doubly protonated complexes are presented in Fig. 6. When the total charge of the complex is +1 or 0, the most stable doubly protonated complex is the (b,x) isomer. We note that the $\text{MH}(\text{b})\text{H}(\text{t})$ complex with the bdt ligand is only 5 kJ mol^{-1} less stable than the $\text{MH}(\text{b})\text{H}(\text{x})$ complex. The $\text{MH}(\text{b})\text{H}(\text{t})$ becomes the most stable isomer when the total charge of the complex is -1 . For all examined doubly protonated complexes, the (t_1, t_2) isomers have a significantly higher free energy than the other isomers. On the other hand, the isomers in which protons form dihydrogen are only $20\text{--}30\text{ kJ mol}^{-1}$ higher in energy than the most stable complexes, which makes them possibly available as a transient structure from which the hydrogen molecule is released.

Selected bond lengths of the most stable doubly protonated complexes are listed in Table 5. They are similar to those of the bridging isomers of the singly protonated complexes. The exception is Fe–Fe bond length of the $\text{MH}(\text{b})\text{H}(\text{t})^-$ complex, which is $0.44\text{ \AA}$ shorter than the one of the $\text{MH}(\text{b})^{2-}$ complex. We show below that this affects the infrared spectrum of the $\text{MH}(\text{b})\text{H}(\text{t})^-$ complex.

Partial charges of selected atoms in the doubly protonated complexes are given in Table 6. The bridging hydrogen atom is

Table 5 Selected bond lengths (in $\text{\AA}$) of the doubly protonated complexes in the three different oxidation states and with the two different bridging bdt and bds ligands

Bond	$\text{MH}(\text{b})\text{H}(\text{x})^+$		$\text{MH}(\text{b})\text{H}(\text{x})$		$\text{MH}(\text{b})\text{H}(\text{t})^-$	
	bdt	bds	bdt	bds	bdt	bds
$\text{Fe}_1\text{--Fe}_2$	2.68	2.70	2.53	2.55	3.06	3.13
$\text{Fe}_1\text{--X}_1$	2.27	2.37	2.34	2.44	2.37	2.46
$\text{Fe}_1\text{--X}_2$	3.30	3.31	3.91	4.03	3.81	3.94
$\text{Fe}_2\text{--X}_1$	2.29	2.40	2.30	2.40	2.34	2.43
$\text{Fe}_2\text{--X}_2$	2.33	2.43	2.36	2.45	2.35	2.45
$\text{Fe}_1\text{--H}_1$	1.68	1.68	1.64	1.65	1.57	1.58
$\text{Fe}_2\text{--H}_1$	1.63	1.64	1.72	1.71	1.97	1.98

Table 6 Partial atomic charges (in atomic units) of the doubly protonated complexes

Atom	$\text{MH}(\text{b})\text{H}(\text{x})^+$		$\text{MH}(\text{b})\text{H}(\text{x})$		$\text{MH}(\text{b})\text{H}(\text{t})^-$	
	bdt	bds	bdt	bds	bdt	bds
Fe_1	−0.21	−0.26	−0.56	−0.60	−0.65	−0.67
Fe_2	−0.51	−0.56	−0.49	−0.54	−0.35	−0.39
X_1	0.17	0.32	0.14	0.29	0.02	0.16
X_2	0.28	0.44	0.18	0.33	−0.14	−0.07
H_1	−0.07	−0.07	−0.01	−0.02	−0.04	−0.04
H_2	0.21	0.15	0.18	0.13	0.01	0.01

found to be always negatively charged, which implies that it has significant hydride character. On the other hand, the hydrogen atoms bound to a chalcogen atom are strongly positive, which makes them unattractive for reaction with acidic protons. The hydrogen atom in the terminal position of the $\text{MH}(\text{b})\text{H}(\text{t})^-$ complex has a very small positive charge.

The infrared spectra of the most stable doubly protonated isomers are shown in Fig. 7 for the frequency range from 1600 to 2200 cm^{-1} . The presented spectral region does not include the X–H stretching mode, which is active at approximately 2540 cm^{-1} with medium intensity. The Fe–H stretching mode of the $\text{MH}(\text{b})\text{H}(\text{t})^-$ complex has a peak at 1843 cm^{-1} , but its intensity is very small and thus it is not useful for assignment of the isomer (see Fig. 7(c)). The CO stretching bands of the $\text{MH}(\text{b})\text{H}(\text{x})^+$ and $\text{MH}(\text{b})\text{H}(\text{x})$ isomers have similar intensities and positions to those of the singly protonated complexes. Lu *et al.*²⁴ reported the following CO stretching frequencies of

Fig. 6 Optimized geometries of the most stable isomers of doubly protonated complexes in three different oxidation states.

Fig. 7 Computed infrared spectra of the doubly protonated complexes with the bdt (black stick lines) and bds (red stick lines) ligands in the frequency range of the CO stretching bands: (a) $\text{MH}(\text{b})\text{H}(\text{x})^+$, (b) $\text{MH}(\text{b})\text{H}(\text{x})$, and (c) $\text{MH}(\text{b})\text{H}(\text{t})^-$.

the MH_2 complex: 2070 (m), 2024 (vs), 2005 (s), 1973 (sh), and 1780 (w) cm^{-1} in CH_2Cl_2 solution. Our calculated frequencies of the $\text{MH}(\text{b})\text{H}(\text{x})$ complex with the bdt ligand at 2073 (m), 2032 (vs), 2011 (s), 2007 (s), 1992 (m), and 1814 (m) cm^{-1} nicely match with the experimental ones. Thus we support the conclusion of Liu *et al.*²⁴ that the protonation of the MH^- complex takes place at the sulfur atom. The CO modes of the $\text{MH}(\text{b})\text{H}(\text{t})^-$ complex are active above 1950 cm^{-1} , which is very distinct from the $\text{MH}(\text{b})^{2-}$ spectrum.

3.4 Triply protonated complexes

Here we consider three possible isomers of a triply protonated complex. Using our previous labels, these are (b,t,x), (t_1, t_1, x), and (t_1, t_2, x). The optimized geometries of the most stable isomers of the triply protonated complexes are shown in Fig. 8. Selected computed bond lengths, atomic charges and infrared spectra of the CO stretching modes are given in Tables 7, 8 and Fig. 9, respectively. The most stable isomer in all reduced states is the (b,t,x) complex, which is in line with the most stable doubly protonated isomers, (b,x) and (b,t), seen before. The $\text{MH}(\text{x})\text{H}(\text{t}_1)\text{H}(\text{t}_1)^+$ and $\text{MH}(\text{x})\text{H}(\text{t}_1)\text{H}(\text{t}_1)$ isomers are 31 and 36 kJ mol^{-1} less stable than the $\text{MH}(\text{b})\text{H}(\text{t})\text{H}(\text{x})^+$ and $\text{MH}(\text{b})\text{H}(\text{t})\text{H}(\text{x})$ complexes with the bdt ligand, respectively.

Comparison of the bond lengths of $\text{MH}(\text{b})\text{H}(\text{x})$ and $\text{MH}(\text{b})\text{H}(\text{t})\text{H}(\text{x})^+$ as well as $\text{MH}(\text{b})\text{H}(\text{t})^-$ and $\text{MH}(\text{b})\text{H}(\text{t})\text{H}(\text{x})$ reveals that the Fe–Fe bond shrinks but the Fe–X bonds elongate upon protonation of doubly protonated complexes. As was the case for the doubly protonated complexes, the charges of the bridging hydride, the terminal hydrogen atom,

Fig. 8 Optimized geometries of the most stable isomers of triply protonated complexes.

Table 7 Selected bond lengths (in Å) of the triply protonated complexes

Bond	$\text{MH}(\text{b})\text{H}(\text{t})\text{H}(\text{x})^+$		$\text{MH}(\text{b})\text{H}(\text{t})\text{H}(\text{x})$	
	bdt	bds	bdt	bds
Fe ₁ –Fe ₂	2.71	2.75	2.96	3.02
Fe ₁ –X ₁	2.28	2.38	2.34	2.44
Fe ₁ –X ₂	3.44	3.49	3.48	3.52
Fe ₂ –X ₁	2.28	2.39	2.31	2.43
Fe ₂ –X ₂	2.33	2.43	2.41	2.47

Table 8 Partial atomic charges (in atomic units) for selected atoms of the triply protonated complexes

Atom	$\text{MH}(\text{b})\text{H}(\text{t})\text{H}(\text{x})^+$		$\text{MH}(\text{b})\text{H}(\text{t})\text{H}(\text{x})$	
	bdt	bds	bdt	bds
Fe ₁	−0.61	−0.63	−0.63	−0.65
Fe ₂	−0.48	−0.54	−0.37	−0.43
S ₁	0.21	0.37	0.08	0.21
S ₂	0.29	0.46	0.20	0.37
H ₁	−0.04	−0.05	−0.06	−0.06
H ₂	0.01	0.00	0.02	−0.04
H ₃	0.20	0.14	0.18	0.12

and the chalcogen-bound hydrogen atom are negative, close to zero, and positive, respectively.

Infrared spectra of carbonyl stretching modes of the $\text{MH}(\text{b})\text{H}(\text{t})\text{H}(\text{x})^+$ and $\text{MH}(\text{b})\text{H}(\text{t})\text{H}(\text{x})$ complexes are very similar to those of $\text{MH}(\text{b})\text{H}(\text{x})$ and $\text{MH}(\text{b})\text{H}(\text{t})^-$. Comparing the computed infrared frequencies of the $\text{MH}(\text{b})\text{H}(\text{t})\text{H}(\text{x})^+$ isomer (2135 (s), 2100 (vs), 2088 (m), 2087 (m), 2051 (m), 2050 (m)) with the experimental ones (2132 (s), 2097 (vs), 2078 (s), 2041 (m)) in CH_2Cl_2 solution²⁴ we note good agreement. Thus, we agree with Liu *et al.*²⁴ that the protonation of the $\text{MH}(\text{b})\text{H}(\text{x})$ isomer occurs at the terminal position.

3.5 Electrochemical properties

Fig. 10 shows a thermodynamic map of the most stable isomers, with horizontally the standard reduction potentials (SRPs) and vertically the acidities (pK_a s) connected to the reduction and protonation transitions between the complexes. Generally, by going from left to right in the map, the SRP decreases and the pK_a increases. The same holds for going from

Fig. 9 Computed infrared spectra of the triply protonated complexes with the bdt (black stick lines) and bds (red stick lines) ligands of the CO stretching bands: (a) $\text{MH}(\text{b})\text{H}(\text{t})\text{H}(\text{x})^+$, and (b) $\text{MH}(\text{b})\text{H}(\text{t})\text{H}(\text{x})$.

Fig. 10 Thermodynamic map with calculated standard reduction potentials (horizontal arrows) and pK_a s (vertical arrows) of all examined complexes with bdt and bds (in brackets) ligands.

bottom to top in the map. These trends have a simple electrostatic basis; it is in general easier to take a proton from a more positively charged complex and to take an electron from a more negatively charged complex. Nevertheless, the exact values are related to electron affinities and bond formation energies, which may not obey simple patterns.

Let us first discuss the thermodynamic properties of the complexes with the bdt ligand. The computed SRP and pK_a values of these complexes are in a very good agreement with the available experimental results. The first and the second SRPs of the catalyst are computed to be -1.31 and -1.25 V relative to the ferrocene electrode, which is very close to the observed

potential of approximately -1.3 V.^{17,18} The third reduction of the unprotonated catalyst appears at a much higher potential of -3.04 V.

The protonated MH^+ complex is reduced at -0.37 V. Liu *et al.* observed this reduction at -0.67 V in CH_2Cl_2 .²⁴ The reduction potential of the neutral MH complex is -0.41 V. It is thus much easier for the MH complex to accept an electron than it is for the neutral M complex. On the other hand, two electron reduction of MH is not so easy as for M, given the MH^- SRP of -2.13 V. The latter number nicely matches the experimental value of approximately -2.1 V.¹⁸ The reduction potential of MH_2 is -1.10 V, which is more negative than the reduction potential of MH, but also somewhat positive with respect to the reduction potential of the M complex.

The computed pK_a of the MH complex is 11.7. This value is within range of the experimentally estimated $\text{pK}_a < 12.7$.²³ Furthermore, the computed pK_a of MH^- is 25.9, in agreement with the observation of Felton *et al.*¹⁸ that no catalysis was observed with acids weaker than $\text{pK}_a = 25.5$ in the applied potential range. Thus, very weak acids are not able to protonate the M^{2-} anion directly. With very weak acids, the protonation of electrochemically generated catalyst anions can be achieved by employing much larger overpotentials to produce the M^{3-} anion. The M^{3-} anion is more basic than the M^{2-} anion by 15.4 pK_a units. The M^{2-} and MH^{2-} anions are almost equally basic. The same holds for the MH^- and MH_2^- complexes and for MH_2 and MH_3 complexes. This shows that only strong acids can protonate the MH^- and MH_2^- complexes, because the pK_a 's of MH_2 and of MH_3 are 7.5 and 7.1, respectively.

Exchange of the sulfur atoms by selenium atoms increases the basicity of the iron atoms, which is favorable for the protonation of the M, M^- , M^{2-} , and MH_2 complexes. For the other complexes, the S to Se substitution is not favorable for protonation, because the protonation occurs at the chalcogen atom, which has a decreased electron density after exchange and thus a lower proton affinity. The exceptions are the M^{3-} and MH^{2-} complexes, for which the partial charge analysis showed that the exchange of sulfur by selenium does not increase the electron density at the iron atoms. In addition, most of the examined reduction potentials become more positive upon chalcogen exchange, which improves the performance of the catalyst. The largest change is found for the reduction of the M^{2-} complex with an increased SRP of 0.26 V. Significant changes are also found for the reduction of MH^- and of MH_2 with increases of 0.07 and 0.15 V. The largest decrease of the SRP is computed for the MH species (-0.21 V). The reduction potential of the M complex changes by only -0.02 V.

The computed thermodynamic map reveals several interesting features of the catalyst. First, a very strong acid is necessary for the protonation of the neutral complex. The chalcogen substitution decreases the acidity of MH^+ complex by two pK_a units. It is likely that the exchange of selenium by tellurium atoms would additionally ease the protonation of the neutral complex, but the catalytic pathway that starts with the protonation of the neutral complex would still be available only with very strong acids. Secondly, the triply protonated complexes can be formed only

with strong acids, which is not favorable for proton reduction. Third, the reduction at potentials below approximately -3 V might enable proton reduction from acids with a pK_a smaller than 26. Fourth, it remains still unclear whether the second proton reacts directly from the solvent with the hydride in the MH^- and MH^{2-} complexes to form molecular hydrogen or it first binds to the complex to form a doubly protonated species. The proton's partial atomic charge is positive in the MH^- complex, but negative in the MH^{2-} complex. Thus, it is likely that the MH^{2-} complex reacts directly with a proton donor. On the other hand, the MH^- complex might be first protonated to form the MH_2 complex. In the latter case, molecular hydrogen is formed by a direct reaction between the negatively charged hydrogen atom in the bridging position and positively charged hydrogen atom on the chalcogen atom.

4 Conclusions

We have carried out an extensive density functional theory-based study of the diiron benzenedithiolato and the benzenediselenato carbonyl catalysts and its reduced and protonated complexes that can be formed by addition of up to three electrons and/or protons. The calculated structural parameters, infrared spectra and thermodynamic properties are in very good agreement with the available experimental data, which justifies the employed computational approach. The substitution of sulfur atoms by selenium atoms increases the electron density at the iron atoms, giving them a higher proton affinity, but decreases the electron density at the chalcogen atoms, which results in a lower proton affinity at those atoms. Incorporation of electron-withdrawing substituents on the benzene ring of the bdt ligand was previously shown to decrease the reduction potential of the catalyst, meanwhile maintaining the reversible two-electron feature of the primary reductions.¹² Yet, these substituents made the complex less basic and harder to protonate. Here, we showed that the basicity of the singly and doubly reduced complexes can be increased by the chalcogen atom substitution, which provides a new opportunity to tune the catalytic properties of aromatic ligands. In the most stable singly protonated complexes the proton binds in a bridging position to both iron atoms, irrespective of the overall oxidation state. With the exception of the MH^+ complex, the proton is always closer to one than to the other iron atom. The most stable isomers of the doubly protonated complexes bind the second proton at the chalcogen atom in the cases of the MH_2^+ and MH_2 complexes, whereas in the case of MH_2^- it binds to iron in a terminal position. The bridging proton is negatively charged in these complexes. Isomers in which the protons reside on the same iron atom are 20 to 30 kJ mol^{-1} less stable than the most stable doubly protonated complexes. The most stable isomers of the triply protonated complexes have the protons located on different binding sites. The catalytic pathway that starts with the protonation of the neutral complex is available only with very strong acids. On the other hand, with very weak acids protons can be reduced at potentials below -3 V.

Conflicts of interest

There are no conflicts to declare.

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