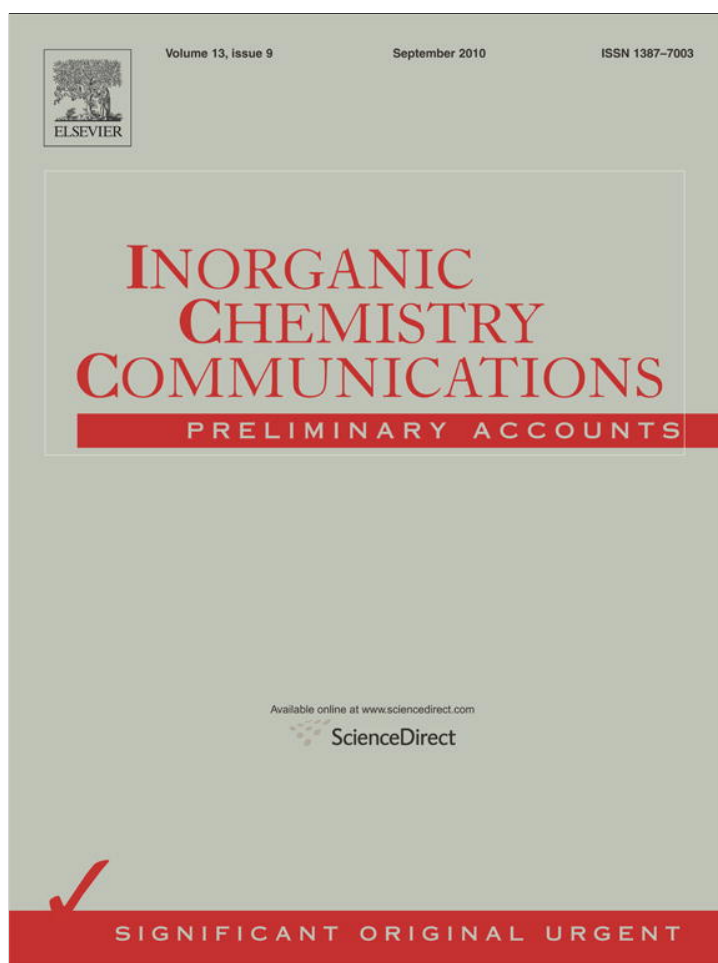


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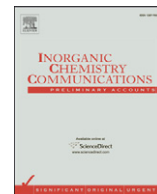
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A rare bond between a soft metal (Fe^{I}) and a relatively hard base (RO^- , R = phenolic moiety)

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ABSTRACT

Reacting a bidentate ligand **H₂L**, 2-(2-methoxybenzyl)-2-methylpropane-1,3-dithiol, with $\text{Fe}_2(\text{CO})_{12}$ formed a diiron hexacarbonyl complex (**1Me**) from which a diiron hexacarbonyl complex (**1H**) pendant with a phenolic group was derived *via in-situ* demethylation. Further deprotonation of complex **1H** gave a diiron pentacarbonyl species (**1**) in which a rare bond between the soft metal Fe^{I} and the relatively hard base phenolate formed, $\text{Fe}^{\text{I}}\text{-OR}$ (R = phenolic moiety). This bonding may be a suitable mimic of the bonding feature, $\{\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}\}\text{R-OH/OH}_2$ found in the [FeFe]-hydrogenase.

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In the past decade, great efforts have been devoted to the bioinorganic chemistry of [FeFe]-hydrogenase in order to understand the enzymatic chemistry of high efficiency in catalysis of both hydrogen evolution and oxidation [1–12]. Modelling the unusual features of the dimetallic centre such as, $\{\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}\}\text{-OH}_2/\text{OH}^-$, “semi-bridging” CO, and proximal connection to a $\{\text{Fe}_4\text{S}_4\}$ -cubane *via* a cysteinate bridge, Fig. 1 (left) [13–15], have been the subject under intensive investigations. Indeed, some synthetic systems mimicked elegantly some of the peculiar enzymatic structural features, for example, a synthetic H-cluster framework [1], a diiron complex with “semi-bridging” CO and an unoccupied “vacant site” at $\{\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}\}$ oxidation states level [10,11]. However, to date model complexes featuring $\{\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}\}\text{-OR}$ or $\{\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}\}\text{-OR}$ (R = organic moiety) moiety have not been reported.

Systems featuring the $\{\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}\}$ oxidation states have been the most accessible in modelling the diiron sub-unit of the enzyme. Assembling a system with $\{\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}\}\text{-OR}$ would be the first step leading to its oxidised form, $\{\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}\}\text{-OR}$ *via* one electron oxidation. Indeed, previous attempts made by using ligands containing carboxylic acid, ether oxygen, and alcoholyl group were unsuccessful [16–19].

Herein, we report a novel bidentate ligand (**H₂L**), 2-(2-methoxybenzyl)-2-methylpropane-1,3-dithiol, its diiron hexacarbonyl complex, $[\text{Fe}_2(\mu\text{-SCH}_2)_2\text{CMe}(\text{CH}_2\text{-}o\text{-C}_6\text{H}_4\text{OMe})(\text{CO})_6]$ (**1Me**), and its

demethylated product, $[\text{Fe}_2(\mu\text{-SCH}_2)_2\text{CMe}(\text{CH}_2\text{-}o\text{-C}_6\text{H}_4\text{OH})(\text{CO})_6]$ (**1H**), which bears a pendant phenolic group. Deprotonation of the pendant phenol led to a species possessing an infrared spectral profile similar to those of other diiron pentacarbonyl complexes reported previously [3,5,8,20]. Infrared spectroscopic analysis, tandem mass spectrometric, and theoretical investigations suggested that this species with an $\text{Fe}^{\text{I}}\text{-OR}$ bond, $[\text{Fe}_2(\mu\text{-SCH}_2)_2\text{CMe}(\text{CH}_2\text{-}o\text{-C}_6\text{H}_4\text{O})(\text{CO})_5]^-$ (**1**), takes the geometry found for other neutral diiron pentacarbonyl complexes reported in the literatures [5,6].

The dithiol ligand (**H₂L**) was prepared *via* a 7-step synthesis, Scheme 1. With the phenol in this ligand protected, complex **1Me** was formed by following a well-established procedure, with a yield over 85%. Demethylation of complex **1Me** with BBr_3 afforded complex **1H** in good yield (*ca.* 60%). In acetonitrile, both complexes show characteristic infrared bands of diiron hexacarbonyl complexes and have nearly superimposable spectral profile since demethylation occurs far away from the Fe–Fe centre. The identities of complexes **1Me** and **1H** were further, unambiguously, confirmed by microanalysis and ^1H NMR spectroscopy. In addition, complex **1Me** was also crystallographically analysed, Fig. 1 (right), showing that the geometry of this complex is essentially identical to other diiron hexacarbonyl complexes reported previously [5,6].

Treatment of a solution of complex **1H** with excess of NaH in MeCN at 0 °C caused distinct change in colour, from light to dark red, and generated a group of new IR absorption bands at 2023.8, 1954.2, 1892.6 cm^{-1} , Fig. 2 (dashed line). On average, the stretching frequency of the newly produced species shifted to low frequency by nearly 60 cm^{-1} compared to its parent complex **1H**. Presumably,

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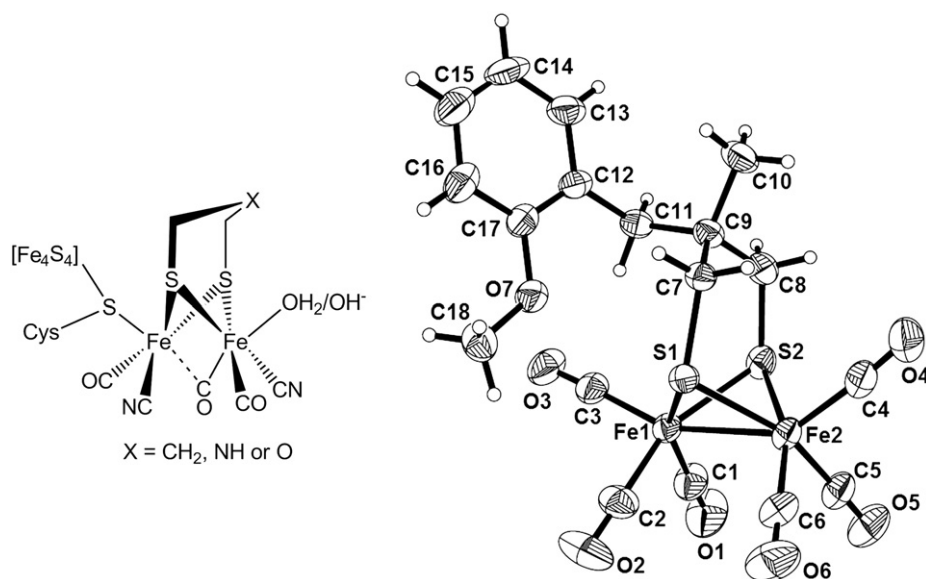
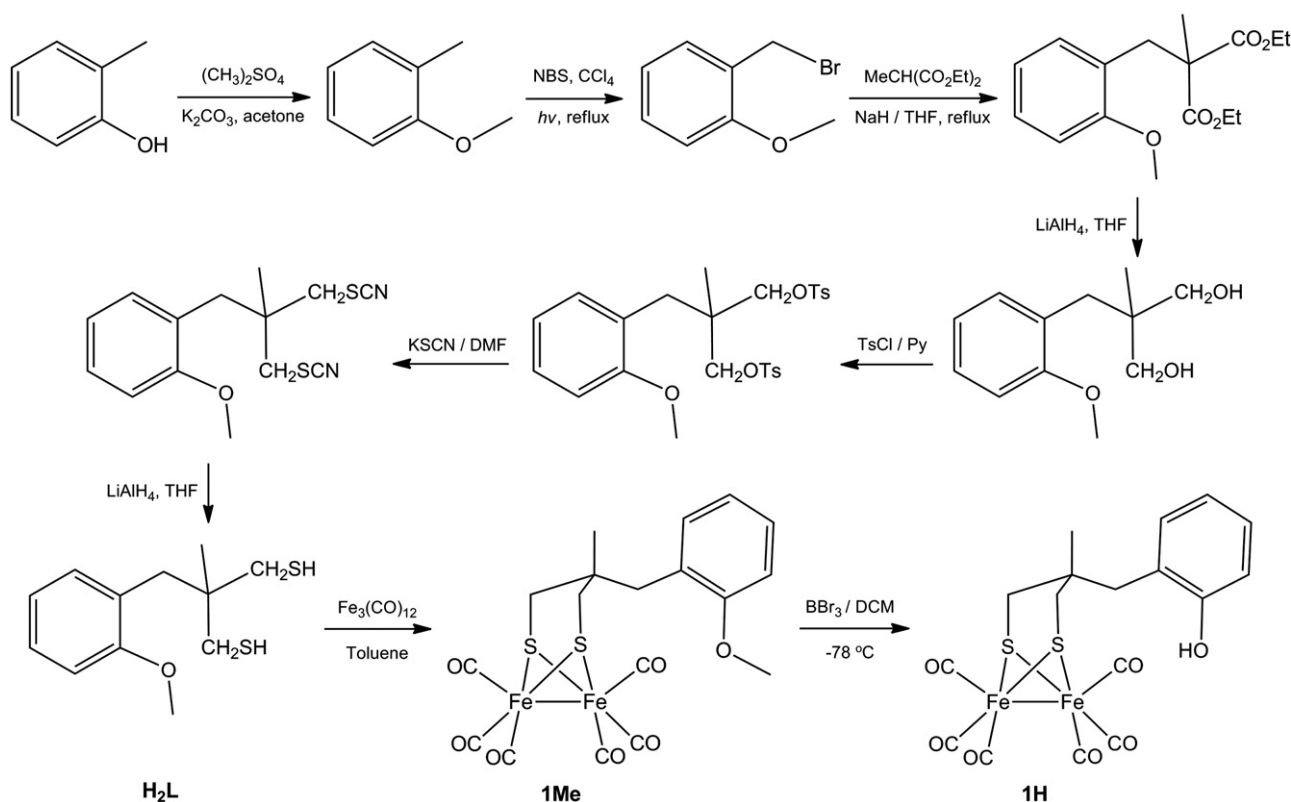


Fig. 1. Schematic view of the H-cluster of the [FeFe]-hydrogenase (left) and crystal structure of complex 1Me (right).

the pendant phenol of **1H** was first deprotonated by NaH to produce an intermediate with a pendant phenolate which then subsequently binds to the proximal iron to form an anionic diiron pentacarbonyl complex by expelling one CO molecule, Scheme 2.

The final product showed characteristic spectral pattern of diiron pentacarbonyl complexes [3,5,8,20]. Plotting the average absorption bands of those diiron pentacarbonyl complexes reported in literatures against those corresponding bands of the proposed complex **1** produces

an excellent linear correlation, Fig. 2. The linear correlation strongly suggests that the final species formed is characterised by a geometry similar to that of other diiron pentacarbonyl complexes [5]. Compared to previously reported diiron pentacarbonyl species [3,5,8,20], these absorption bands of the resultant species show a large “red” shift by about 30 cm⁻¹ on average, Fig. 3, which strongly suggests the binding of the pendant phenolate to the Fe–Fe centre to form a complex featuring a {Fe^IFe^I}-OR core, Scheme 2. Compared to the mimic containing a {Fe₄S₄}-



Scheme 1. Synthetic route leading to ligand **H₂L**, complexes **1Me**, and **1H**.

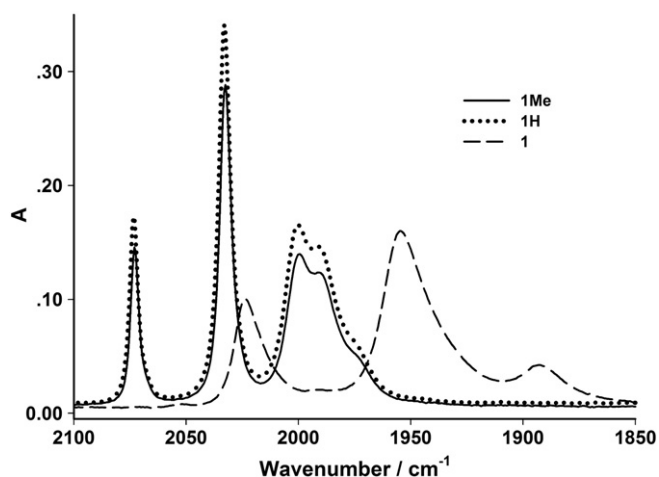


Fig. 2. Infrared spectra of complexes **1Me**, **1H**, and **1**.

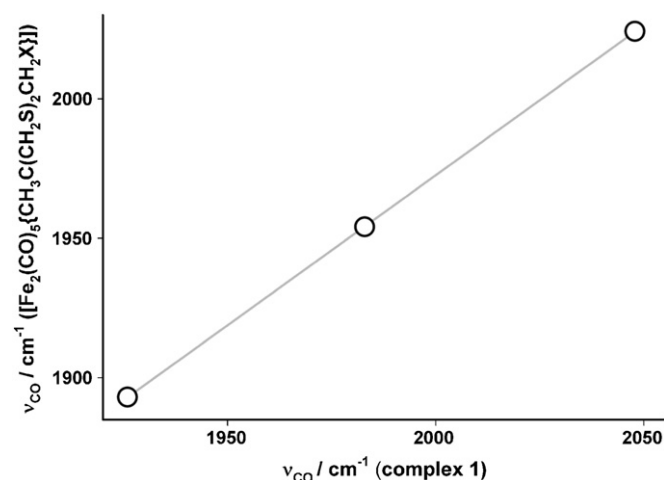


Fig. 3. Plot of average infrared absorption bands of the diiron pentacarbonyl complexes reported in the literature, $[\text{Fe}_2(\mu\text{-SCH}_2)_2\text{CMe}(\text{X})(\text{CO})_5]$ ($\text{X} = \text{CH}_2\text{SMe}$, CH_2NH_2 , pyridin-2-yl) against the corresponding bands of complex **1**.

cubane [1], the absorption bands of the proposed complex **1** are even further downshifted on average by 15 cm^{-1} , which is indicative of a strong electronic effect exerted by the phenolate on the Fe–Fe centre via direct binding.

In addition to the infrared spectroscopic evidence shown above, the identity of the proposed species **1** was further unambiguously established by tandem mass spectrometry and DFT calculations even though characterising the proposed species by NMR spectroscopy and crystallography turned out to be unsuccessful due to the relatively poor stability of such derivative (refer also to Fig. S1). As shown in Fig. S3a, a molecular peak at 477 corresponding to the proposed diiron pentacarbonyl anion **1** is dominant and related fragments, which are obtained by stripping CO off from the parent anion in the manner of one-by-one by using tandem mass spectrometry, are also evident, Fig. S3b–f. Possible dissociation pathways for those observed intermediates are depicted in Fig. S3g.

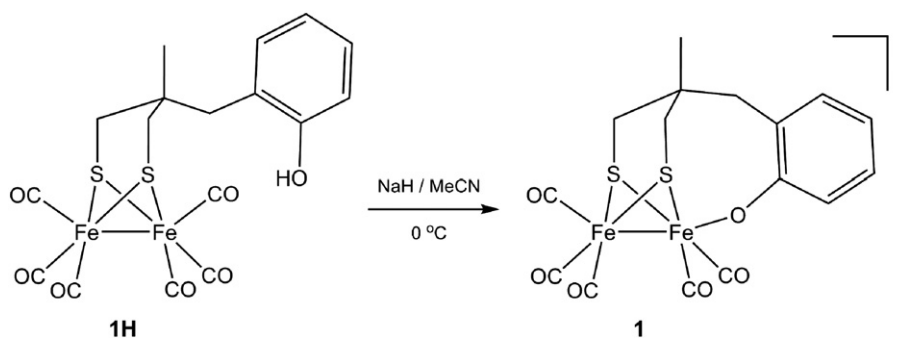
DFT calculations indicate that the reaction leading to species **1** isomer featuring five coordinated CO ligands in which the RO group is directly bound to one iron atom as shown in Fig. 4 is exothermic ($-16.3\text{ kcal mol}^{-1}$). The DFT structure of species **1** is characterised by overall geometry and bonding parameters typical of analogous diiron complexes [3,5,8]. DFT calculations generated IR absorption bands at 2039.1, 1988.6, 1979.5, 1967.3, and 1900.7 cm^{-1} for species **1**, of which the three bands around 1980 cm^{-1} are corresponding to the relatively broad absorption band centred at 1954.2 cm^{-1} observed experimentally, Fig. 2. Plotting the computed against the bands observed experimentally produced a very good linear correlation ($R=0.99$) as shown in Fig. S3. Since the spectroscopic profile of a molecule is closely

correlated to its structure, the observed linear correlation between the computed and experimentally observed bands provides further support for the structural assignment of complex **1**.

In summary, we have described a route leading to a novel phenolate-bound diiron pentacarbonyl anion (**1**), which possesses a rare bond between a soft metal and a relatively hard base, phenolate. Its identity and structural features were established by infrared spectroscopic and tandem mass spectrometric analyses, as well as DFT calculations. The reported synthetic approach may provide a starting point to access mimics for the dimetallic core, $\{\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}\}\text{-OH}_2/\text{OH}^-$, of the enzyme. In the light of the structural and electronic resemblances to the dimetallic centre of the enzyme, the presented phenolate-based complex may be another appropriate system to further explore its bioinorganic chemistry relevant to the diiron sub-unit of the enzyme, in addition to other categories of models investigated intensively in the past decade, that is, complexes featuring $\{\text{Fe}_2\text{S}_2\}$ -core [21–23], aza-containing complexes [24,25], and $\{\text{Fe}_2\text{S}_2\text{X}\}$ -based models ($\text{X} = \text{S}$ or N) [1,5,8,26].

Acknowledgments

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Scheme 2. Conversion of complexes **1H** into **1**.

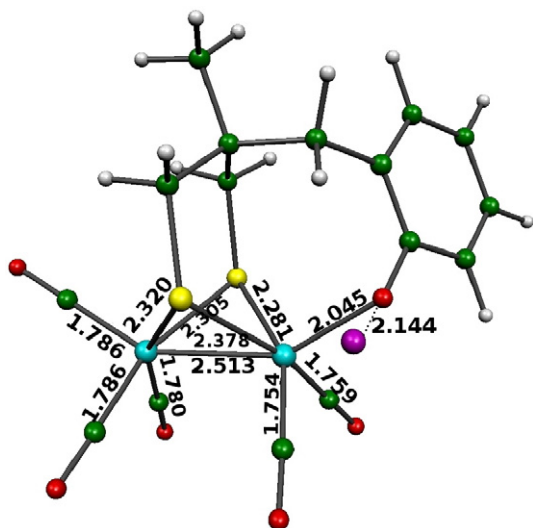


Fig. 4. Structural view of complex **1** with its positioned sodium cation including selected bond lengths (Å) derived from DFT calculations. Colour legends for atoms: turquoise (Fe), purple (Na), yellow (S), red (O), green (C), and grey (H).

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.inoche.2010.06.026.

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