A rare bond between a soft metal (FeI) and a relatively hard base (RO\(^-\), R = phenolic moiety)

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**Abstract**

Reacting a bidentate ligand \(H_2L\), 2-(2-methoxybenzyl)-2-methylpropane-1,3-dithiol, with \(Fe_2(CO)_12\) 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 FeI and the relatively hard base phenolate formed, FeI-OR (R = phenolic moiety). This bonding may be a suitable mimic of the bonding feature, {FeIFeI}R-OH/OH\(^2\) found in the [FeFe]-hydrogenase.

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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 \{FeFe\}_2-OR core, Scheme 2. Compared to the mimic containing a \{Fe₄S₄\}-
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 ($-16.3$ 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, Fe$^{2+}$–OH$_2$/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 Fe$^{2+}$–S$_2$-core [21–23], aza-containing complexes [24,25], and Fe$^{2+}$S$_2$X-based models (X=S or N) [1,5,8,26].

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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.

References