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Influence of the basicity of internal bases in diiron model complexes on hydrides formation and their transformation into protonated diiron hexacarbonyl form

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ABSTRACT

Reaction of 2-(1-(pyridin-2-yl)ethyl)propane-1,3-dithiol with tri-iron dodecacarbonyl afforded a diiron pentacarbonyl complex, $[Fe_2\mathbf{L}(CO)_5]$ (**A** and $\mathbf{H_2L}$ = 2-methyl-2-(1,2,5,6-tetrahydropyridin-2-yl)propane-1,3-dithiol). In the reaction, the pyridinyl ring of the original ligand was partially hydrogenated during the reaction. This complex was fully characterised by using crystallographic, infrared, and NMR spectroscopic techniques. Formation reaction of its bridging hydride and subsequent conversion into its protonated diiron hexacarbonyl complex, $[Fe_2\mathbf{L}(CO)_6]$ ($\mathbf{ACOH^+}$ in which the N atom of **L** is decoordinated and protonated), were experimentally and theoretically investigated. Results for this complex alongside with theoretic investigations into other diiron pentacarbonyl analogues revealed positive correlation of basicity of the internal bases of these investigated complexes to bridging hydrides formation. But subsequent conversion of these bridging hydrides into protonated diiron hexacarbonyl complexes was not solely dictated by the basicity. Protophilicity of the internal base and lability of its coordination with the diiron centre play also an important role as revealed by experimental and theoretic investigations.

1. Introduction

In the past decade, bio-inspired chemistry related to the [FeFe]-hydrogenase [1–2] has attracted tremendous attentions due to its relevance to the production of hydrogen, a possible future clean energy source. Albeit it is still a long journey before achieving artificial systems with efficiency comparable to the metalloenzyme, significant progresses have been made in recent years. These achievements embraced all aspects of the bioinorganic chemistry related to this enzyme [3–26], ranging from structural mimics to mechanistic understandings of the enzymatic catalysis.

In the catalysis of hydrogen evolution, mechanisms of proton transfer, hydride formation, and its conversion, have fundamental importance in understanding the enzymatic catalysis, devising, and synthesising novel artificial systems. Although there are many reports concerning hydride chemistry in modelling the diiron subunit of the H-cluster of the hydrogenase [6,10,27–33], reports describing interactions of bridging hydride with internal pendant base in either the first or second coordinating environment are rare. Recently, Wang, Sun and their co-workers observed that a bridging hydride interacts significantly with a pendant base group in a diiron model complex [34]. Talarmin and his co-workers reported an inter-conversion between a bridging hydride and a pendant base in the second coordinating environment in dichloromethane [35]. Earlier, we reported some diiron pentacarbonyl complexes with an internal base as models for the sub-unit of the enzyme, which, unlike the above systems reported, was bound to one of the iron atoms with some lability, $[Fe_2\mathbf{L}'(CO)_5]$ ($\mathbf{H_2L}'$ = a tridentate ligand with two S ligating atoms and a N-containing base) [36]. Their protonation proceeded in two pathways. The bound base dissociated into a pendant internal base, which was subsequently protonated and diiron hexacarbonyl complex formed consequently by taking up a CO molecule. This pathway is particularly favoured under CO atmosphere. The Fe–Fe bond could also be protonated to form first a bridging hydride, which at the end could transform into a diiron hexacarbonyl complex as shown in Scheme 1 [36].

The formation of bridging hydrides shown in Scheme 1 was mainly confirmed by using infrared spectroscopy. Their NMR resonances were elusive due to their instability while a thioether analogue, $[Fe_2(\mu\text{-}SCH_2)_2CMe(CH_2SMe)(CO)_5]$ [8,37], was stable enough

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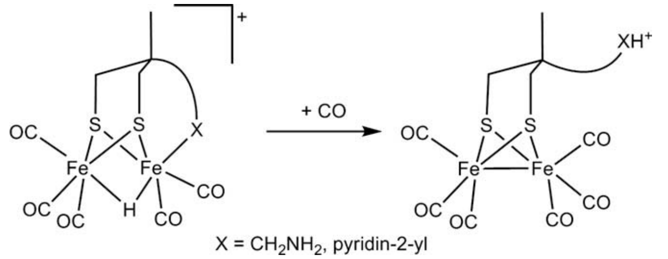

Scheme 1. Conversion of the bridging hydride (left) to the protonated hexacarbonyl complex (right).

to allow such detection. More interestingly, the latter hydride did not convert into diiron hexacarbonyl complex as those shown in Scheme 1. It would be pertinent to assume that the basicity of the bound internal base in both Brønsted–Lowry and Lewis acid–base concepts is associated with formation of the protonated diiron hexacarbonyl complexes as well as this hydride chemistry. But it is not clear how the basicity of the bound internal base correlates to the formation of the protonated diiron hexacarbonyl complexes and the stability of the bridging hydrides.

Recently, re-examination of the reaction which afforded the pyridine-containing diiron pentacarbonyl complex **C** [36] led to the isolation of another diiron pentacarbonyl complex **A**, which is equivalent to the product of partial hydrogenation of the pyridine ring in complex **C**, that is, partial hydrogenation of pyridine-2-yl produced 4*H*-1, 2, 5, 6-pyridin-2-yl. Protonation of this complex gave a rather stable μ-hydride as suggested by its infrared spectroscopy and NMR resonance. With our previously reported μ-hydride chemistry in mind [36], we were prompted to further explore how the stability of these hydrides was dictated and how they converted into protonated diiron hexacarbonyl complexes.

Herein, we report the isolation, characterisation, and protonation of complex **A**. By combining spectroscopic investigations and DFT calculations, correlation of the stability of the hydride of this complex and analogues previously reported [36], to the basicity of their internal bases was explored. In the light of DFT calculations, possible mechanisms for the conversion from the bridging hydrides to the protonated diiron hexacarbonyl complexes were also proposed.

2. Material and methods

2.1. General procedures

All reactions and operations were carried out under argon atmosphere with standard Schlenk techniques. Solvents were dried prior to use according to standard method. The preparation of the tridentate ligand, 2-methyl-2-(pyridin-2-yl) propane-1,3-dithiol (**H$_2$L′**) followed general procedures with minor modification [38]. $Fe_3(CO)_{12}$ was purchased from Sigma Aldrich and $HBF_4{\cdot}Et_2O$ from Alfa Aesar. All chemicals were used as received unless otherwise stated.

FTIR spectra were recorded on Scimitar 2000 (Varian) by using a cell with a spacer of 0.1 mm or KBr pellets. NMR spectra were measured on Bruker AVANCE III (400 MHz) with tetramethylsilane as internal standard. Elemental analyses were performed on a Heraeus CHN–O-Rapid or Elementar Vario MICRO elemental analyzer (Nanjing University).

2.2. Crystal structure analysis

Crystallographic data collection of complex **A** was carried out in the same manner as described elsewhere [39]. Its structure was solved by direct method using SHELXS-97 program [40] and refined on F^2 with XSHELL6.3.1. All non-hydrogen atoms were modelled anisotropically. All hydrogen atoms were positioned geometrically and treated as riding on their parent atoms with C–H distances at 0.93, 0.96, and 0.97 Å for alkenyl, methyl, methylene, and tertiary C–H, respectively, and with $U_{iso}(H) = 1.5\ U_{eq}(C)$ for methyl group but $U_{iso}(H) = 1.2\ U_{eq}(C)$ for the rest of the H atoms.

2.3. DFT calculations

DFT, as implemented in TURBOMOLE 5.7 [41,42], has been employed for determining all the stationary points, *i.e.* intermediates, and transition state structures, of the potential energy hypersurface associated with the reaction coordinate investigated. Functional adopted was the pure B-P86 [43,44] along with a triple-ζ quality basis set, which is a well suited choice for theoretical investigations of the diiron sub-unit of the [FeFe]-hydrogenase and its synthetic analogues [45–47]. Resolution of the Identity (RI) density fitting procedure [48] has allowed to shorten computing time by approximating the two-electron-four-centre integrals (necessary for determination of the Coulomb repulsions) with less computationally demanding three-centre integrals. Second derivatives of the DFT energy with respect to the nuclear positions (potential energy curvature) have also been analytically resolved in order to determine the true nature of all the stationary points located (*i.e.*, minima: all positive eigenvalues of the Hessian matrix; first-order saddle points or transition structure: all positive eigenvalues of the Hessian matrix but one negative eigenvalue associated to the molecular vibration leading to the reactive event). Algorithm employed to search for transient state structure is a pseudo-Newton–Raphson method, implemented with the TRIM [49] procedure and which entails an "eigen-vector-following" move along the PES in the region of the first-order saddle point. Such method performs extremely well only if a "good" guess of the true transition structure is used for the quest. Such good guess is located by freezing all those molecular degrees of freedom forming the reaction step, *i.e.* those bond lengths, angles or torsions which change most during the reaction event. Solvent corrections have been added, when necessary, to data calculated in gas phase. Dielectric constant value, employed for COSMO [50] modelling of polarisation effects deriving from solvent inclusion is 9.1, which correspond to dichloromethane at standard T values.

2.4. Synthesis

2.4.1. $[Fe_2(\mu\text{-}SCH_2)_2C(CH_3)(2\text{-}C_5H_8N)(CO)_5]$, **A**

To a solution of $Fe_3(CO)_{12}$ (0.216 g, 0.429 mmol) in dry toluene (5 ml) was added a solution of the tridentate ligand **H$_2$L′** (0.079 g, 0.40 mmol) in toluene (10 ml) under Ar atmosphere. The mixture was stirred at 110 °C for 4 h until the ligand was completely reacted as indicated by TLC. Removal of the solvent under reduced pressure produced a solid in dark colour which was purified with flash chromatography (eluent:ethyl acetate:hexanes = 1:4). Complex **A** (25 mg, 14%) was collected first and then the previously reported complex **C** (63 mg, 35%) [36]. Removal of the solvents yielded a brown solid. Crystals suitable for X-ray single crystal diffraction analysis was produced by layering hexanes onto its solution in dichloromethane. FTIR (CH_2Cl_2): 2047.9, 1975.2, 1909.2 cm^{-1}. ^1H NMR ($CDCl_3$): 0.82 (s, 3H, $-CH_3$), 1.385 (d, $J = 13.8$ Hz, 1H, –NH), 1.84 (d, $J = 14.4$ Hz, 1H, NC–CH_aH_b), 2.05 (d, $J = 17.0$ Hz, 1H, NC–CH_aH_b), 2.55 (q, 2H, $-NCH_2$), 2.98 (s, 2H, $-SCH_2$), 3.19 (s, 2H, $-SCH_2$), 4.40 (s, 1H, –NCH), 5.31 (d, $J = 10.0$ Hz, 1H, $-CH_a{=}CH_b$), 6.02 (s, 1H, $-CH_a{=}CH_b$). Microanalysis, calc. (found) for $C_{14}H_{15}Fe_2S_2NO_5$ (FW = 452.1): C, 37.19 (37.10); H, 3.12 (3.28); N, 3.10 (3.22)%.