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Catalytic disproportionation of hydrazine by thiolate-bridged diiron complexes



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GRAPHICAL ABSTRACT



Redox potential

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ABSTRACT

Treatment of a thiolate-bridged diiron complex $[N_2S_2FeClFe(MeCN)Cp^*][PF_6]$ (1, $Cp^* = \eta^5-C_5Me_5$, $N_2S_2 = N_iN^2$ -dimethyl-3,6-diazanonane-1,8-dithiolate) with CO or 'BuNC resulted in ligand exchange to facilely generate $[N_2S_2FeClFeLCp^*][PF_6]$ (2, L = CO; 3, $L = {}^{tBuNC}$). Further electrochemical studies indicate the coligand has an obvious influence on the redox properties of these complexes. Importantly, these complexes with different redox behaviors show distinct catalytic reactivity toward the disproportionation of hydrazine into ammonia.

1. Introduction

Nitrogenase assumes great importance in nature for catalyzing the reduction of dinitrogen (N_2) to ammonia (NH_3) under ambient conditions [1]. Although the active center has been unveiled as a complicated [MoFe₇S₉C] cluster named FeMo-cofactor [2,3], the detailed mechanism of nitrogen fixation was still unclear. During the past two decades, results of computational and experimental chemistry suggest the diiron center in the "belt" region of the FeMo-cofactor is very likely to be the binding and activation site of N₂ and other substrates [4–8].

Recently, crystallographic analysis clearly uncovered the structure of the FeMo-cofactor in CO-inhibited state, in which CO is bridged between the two iron centers in the waist region of the FeMo-cofactor [9]. The coordination of a bridging CO leads the FeMo-cofactor to lose its intrinsic three-fold symmetry and obtain a more asymmetrical structure, which is likely responsible for the change of catalytic properties of nitrogenase [10]. As expected, further results of activity examination reveals that CO-inhibited nitrogenase cannot reduce acetylene to ethylene [9].

Because CO is an isoelectronic species of N2 and noncompetitive

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Received 28 October 2019; Received in revised form 16 December 2019; Accepted 17 December 2019 Available online 23 December 2019 1387-7003/ © 2019 Elsevier B.V. All rights reserved. inhibitor, studies on interaction of diiron nitrogenase mimics with CO are of significance to reveal potential nitrogen fixation mechanism. To date, plenty of nitrogenase mimics were reported to be good promoters for nitrogen fixation and functionalization [11–15], N–N bond cleavage of hydrazine [16–20], CO reduction [21–22] and so on. However, there is no reaction system known to focus on how CO as inhibitor affects the catalytic activity related to nitrogenase, especially with respect to the transformation of hydrazine into NH₃.

Herein, we report the synthesis and characterization of two thiolatebridged diiron complexes with the coordination of CO or ^tBuNC. Electrochemical measurements indicated CO and ^tBuNC as strong donors have a remarkable influence on the redox properties of diiron complexes. Furthermore, these differences in electrochemical behaviors determine their catalytic ability of the disproportionation of hydrazine to release NH₃.

2. Results and discussion

Given the lability of CH₃CN as a ligand, we chose a reported complex $[N_2S_2FeClFe(MeCN)Cp^*][PF_6]$ (1, $Cp^* = \eta^5 - C_5Me_5$, $N_2S_2 = N_1N' - N_2S_2$ dimethyl-3,6-diazanonane-1,8-dithiolate) as reaction precursor [23]. As shown in Scheme 1, treatment of 1 with 1 atmosphere of CO in CH₂Cl₂ from -78 °C to room temperature generated a thiolate-bridged diiron complex [N₂S₂FeClFe(CO)Cp*][PF₆] (2) as a green powder in 84% yield. Complex 2 exhibits excellent solubility in CH₂Cl₂ and CH₃CN, but cannot dissolve in THF. This product was fully characterized by spectroscopy and X-ray crystallography. The electrospray ionization highresolution mass spectrum (ESI-HRMS) of complex 2 shows an expected molecular peak of 516.0431 (calcd 516.0423) for $[2-PF_6]^+$, which confirms the substitution of MeCN by CO. In the infrared (IR) spectrum of **2**, a diagnostic strong absorption band at 1975 cm^{-1} is observed, which further confirms the existence of CO. In addition, this value indicates the CO group is coordinated to the iron center in a terminal endon coordination mode, which is very close to that of nitrogenase in high CO concentration (1973 cm^{-1}) [24] and markedly higher than that of nitrogenase in low CO concentration (1904 cm⁻¹) [25]. Compared with reported thiolate-bridged diiron [26,27] or iron-nickel [28-30] CO complexes with similar coordination sphere, the CO vibration frequency of **2** is significantly higher, which indicates the CO ligand is less activated by the iron center. The formal oxidation states of the two iron centers in **2** are +2 and +3, respectively, which indicates there is at least one unpaired electron. Based on this understanding, we speculated complex **2** should be a paramagnetic species. As we expected, the 1 H NMR spectrum of 2 shows a characteristic broad peak at -32.11 ppm in the high field, which exhibits obvious paramagnetic shift. This resonance may be assigned to the proton signals of the five methyl groups in the Cp* ligand, however, further accurate assignments for other signals are difficult. Furthermore, the magnetic susceptibility measurement of complex 2 in CH₂Cl₂ solution was conducted at room temperature by the Evans method. The value of effective magnetic moment of complex 2 is 5.84 $\mu_{\rm B}$, which indicates complex 2 is in an S = 5/2 ground state at room temperature.

Crystals suitable for X-ray diffraction of **2** were obtained by slow diffusion of *n*-hexane into a dichloromethane solution of **2**. As shown in Fig. 1, crystallographic analysis of **2** reveals that the two iron centres have completely different coordination geometry. The iron of the



Fig. 1. ORTEP (ellipsoids at 50% probability) diagram of complex 2. All hydrogen atoms and the PF_6^- anion are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Fe1–Fe2 3.0676(5), Fe1–S1 2.3997(8), Fe1–S2 2.3727(8), Fe2–S1 2.2526(7), Fe2–S2 2.2477(7), Fe1–Cl1 2.2118(8), Fe2–C1 1.766(3), C1–O1 1.137(3), Fe2–Cp* 1.7608(3), Fe1–S1–Fe2 82.44(2), Fe1–S2–Fe2 83.15(2), S1–Fe1–S2 93.35(3), S1–Fe2–S2 100.97(3), Fe2–C1–O1 176.6(3), S1–Fe1–Cl1 106.35(3), S2–Fe1–Cl1 111.19(3).

{LFeCl} moiety resides above the N₂S₂ plane and capped with a chloride group at apical position. The iron of the {Cp*Fe} moiety is linked to the {LFeCl} moiety through two bridging thiolates of the N₂S₂ ligand. The {Cp*Fe} moiety of **2** possesses a terminal CO ligand with the C–O distance of 1.137(3) Å, which is slightly shorter than those of reported thiolate-bridged diiron [27,31] or iron-nickel [28] complexes. The Fe1–Fe2 distance decreases from 3.1152(8) Å in **1** to 3.0676(5) Å in **2**, which indicates that the two iron centers are more electron-deficient upon the coordination of a better π -acceptor ligand (CO).

Furthermore, we also examined the reactivity of complex 1 with ^tBuNC under similar conditions. After addition of 1 equiv. of ^tBuNC into a CH₂Cl₂ solution of 1 at room temperature, the solution color changed from dark green to brownish yellow. As shown in Scheme 2, the labile MeCN was smoothly replaced by one ^tBuNC group to afford a thiolatebridged diiron complex [N₂S₂FeClFe(^tBuNC)Cp*][PF₆] (3) in 73% yield as a yellow powder. The product was also characterized by spectroscopy and X-ray crystallography.

The ESI-HRMS of complex **3** shows an anticipated molecular peak of 571.1213 (calcd. 571.1208) for $[\mathbf{3}-\mathrm{PF}_6]^+$, which confirms the cationic composition of complex **3**. In the IR spectrum of **3**, a diagnostic strong absorption band at 2137 cm⁻¹ attributed to the N=C bond stretching vibration was observed, which confirms the existence of 'BuNC in a terminal end-on coordination fashion. This value is located at the common range of the N=C bond stretching vibration frequency in known thiolate-bridged diiron and diruthenium complexes [32–35]. The ¹H NMR spectrum of **3** also shows a broad peak at -41.32 ppm. The magnetic susceptibility measurement of complex **3** in CH₂Cl₂ solution was conducted at room temperature by the Evans method. The value of effective magnetic moment of complex **3** is 5.98 $\mu_{\rm B}$, which suggests complex **3** is also in an S = 5/2 spin state.

Using the same method, crystals suitable for X-ray diffraction of **3** were also obtained. Crystallographic analysis of **3** (Fig. 2) reveals that



2

Scheme 2. Synthesis of complex 3.



Fig. 2. ORTEP (ellipsoids at 50% probability) diagram of complex **3**. All hydrogen atoms and the PF_6^- anion are omitted for clarity. Selected bond distances (Å) and bond angles (deg): Fe1–Fe2 3.0830(14), Fe1–S1 2.3940(19), Fe1–S2 2.4313(19), Fe2–S1 2.2426(19), Fe2–S2 2.2509(19), Fe1–Cl1 2.236(2), Fe2–Cl 1.848(7), C1–N1 1.145(8), N1–C2 1.467(9), Fe2–Cp* 1.7587(10), Fe1–S1–Fe2 83.28(6), Fe1–S2–Fe2 82.27(6), S1–Fe1–S2 92.56(6), S1–Fe2–S2 101.80(7), Fe2–C1–N1 177.0(6), S1–Fe1–Cl1 114.58(9), S2–Fe1–Cl1 107.11(8).

the iron of the {Cp*Fe} moiety features a ^tBuNC ligand with the C1–N1 distance of 1.145(8) Å, which is close to those of thiolate-bridged diiron ^tBuNC complexes [27,31,34] and some heteronuclear complexes with {Cp*Fe(^tBuNC)} fragment [32]. The Fe1–Fe2 distance in **3** is 3.0830(14) Å, which suggests that ^tBuNC is a medium π -acceptor ligand to this {Fe₂S₂} system compared with MeCN and CO.

One step further, the redox behaviors of these two complexes were investigated by the cyclic voltammetry for evaluating the effect of the change of co-ligands (CO for 2 and ^tBuNC for 3). The cyclic voltammogram of complex 2 in CH₂Cl₂ solution (Fig. 3 red spectrum) shows two reversible redox waves. The first redox event at $E_{1/2}^{\text{ox}} = 0.52 \text{ V}$ corresponds to an Fe^{II/III} (coordinated with Cp*) couple, which is significantly more positive than that of 1 ($E_{1/2}^{ox} = 0.13$ V) [23]. We speculated the potential shift of the redox wave is mainly caused by the stronger π back-bonding interaction between the iron center and CO donor. It helps to stabilize the electrons of the Fe center and thus increase the redox potential. The second redox wave at $E_{1/2}$ $_{2}^{red} = -0.49$ V corresponds to an {LFeCl}^{III/II} redox couple, which is ca. 0.57 V less negative than that of 1 indicates that complex 2 $(Fe^{III}Fe^{II})$ is much easier to be reduced than 1 to generate "Fe^{II}Fe^{II}" speices. The cyclic voltammogram of complex 3 in CH₂Cl₂ solution (Fig. 3 blue spectrum) also shows two reversible redox waves ($E_{1/2}^{ox} = 0.29 \text{ V}, E_{1/2}^{\text{red}} = -0.95 \text{ V}$), which are closer to those of complex 1 and still much less positive than those of complex 2.

In view of the basic understanding of the effect in redox properties of the co-ligands, we next explored the differences of these complexes in



Fig. 3. Cyclic voltammograms of complexes 1, 2 and 3, measured in 0.1 M nBu_4NPF_6 in CH_2Cl_2 at 100 mV/s and internally referenced to Fc/Fc^+ .

catalyzing redox reactions. Choosing the disproportionation of hydrazine as a model reaction, we examined the catalytic activity of these complexes possessing different redox properties. Stirring the CH₃CN solution of complex 1 with 20 equiv. of hydrazine at room temperature afforded ammonia in 56% yield (Eq. (1); Table 1, entry 1). When changing the catalyst loading from 5 mol% to 2 mol% or 1 mol%, the yield of ammonia remarkably reduced. However, there is no obvious change in the turnover number (see Table S4). Reactions of complexes 2 and 3 with hydrazine were also performed under the same conditions, and the yields of ammonia were 11% and 32%, respectively (Eq. (1); Table 1, entries 2 and 3). The results show that complex 1 exhibits the best reactivity toward disproportionation of hydrazine to generate ammonia. In sharp contrast, complexes 2 and 3 have poor catalytic activity. In previous studies [36], the highly oxidized Fe species was proposed to be an important intermediate during the cleavage of the N-N bond in hydrazine. Hence, since complex 1 has the lowest oxidation potential among them, it is the most oxidizable to reach a high oxidation state, which may be the rate-limiting step during the catalysis. For 2 and 3, affected by the co-ligands (CO and ^tBuNC), their oxidation potentials become more positive, resulting in the relatively weak catalytic ability. Detailed mechanism of the catalyzed reactions

Tuble 1

Catalytic	disproportionation Cat: [FeFe]	of	hydrazine	by	[FeFe]	complex-
es. ^a 3 N ₂ H ₄	CH ₃ CN, rt, 12 h	NH3 +	N ₂ (eq	1)		

Entry	[FeFe] complex	NH ₃ /yield (%) ^b	N ₂ /yield (%) ^c	TON
1		56	61	11.2
2		11	24	2.2
3		32	40	6.4

^a N₂H₄ (0.5 mmol), [FeFe] (25 μmol, 5 mol%), CH₃CN (5 mL), rt, 12 h.

 $^{\rm b}~$ The yields of $\rm NH_3$ were determined by $^1\rm H$ NMR analysis

^c The yields of N₂ were determined by GC.

promoted by these three complexes is still under investigation.

3. Conclusions

In conclusion, two thiolate-bridged diiron CO and 'BuNC complexes were synthesized and characterized by spectroscopy and crystallography. Due to the interaction between the iron centers and inhibitors (CO and 'BuNC), electrochemical properties of these complexes were obviously affected, which is evidenced by cyclic voltammetry. Further investigation on the catalytic activity demonstrates the thiolate-bridged diiron complex possessing the higher oxidation potential can serve as a relatively poor promoter for the disproportionation of hydrazine, which is in good agreement with the inhabitation effect of CO or 'BuNC.

4. Experimental section

4.1. General procedures

All manipulations were routinely carried out under an argon atmosphere, using standard Schlenk-line techniques. All solvents were dried and distilled over an appropriate drying agent under argon. Complex [N₂S₂FeClFe(MeCN)Cp*][PF₆] (1) was prepared according to the literature [23]. ¹BuNC (Energy Chemical), CO (Junfeng Gas) and hydrazine (Aldrich) were used without further purification.

4.2. Spectroscopic measurements

The ¹H NMR spectra were recorded on a Bruker 400 Ultra Shield spectrometer. Infrared spectra IR spectra were recorded with a NEXVSTM FTIR spectrometer. ESI-HRMS were recorded on an HPLC/Q-Tof microspectrometer. Elemental analyses were performed on a Vario EL analyzer. Solution phase magnetic measurements were performed by the Evans method [37]. Cyclic voltammetry experiments were carried out with a three-electrode cell under argon at room temperature. The working electrode was a glassy carbon disk (diameter 3 mm), the reference electrode was a nonaqueous Ag/Ag⁺ electrode, the auxiliary electrode was a platinum wire, and the supporting electrolyte was 0.1 M ⁿBu₄NPF₆ in CH₂Cl₂. All potentials reported herein are quoted relative to the FeCp₂/FeCp₂⁺ couple. Gas chromatography was performed with a Techcomp GC7900 gas chromatography instrument with argon as the carrier gas and a thermal conductivity detector.

4.3. X-ray crystallography procedures

Single-crystal X-ray diffraction studies were carried out on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were performed using the SADABS program [38]. All of the structures were solved by direct methods and refined by full-matrix least-squares based on all data using F2 using SHELXTL 2014 [39,40]. All of the non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were generated and refined in ideal positions.

4.4. Synthesis of $[N_2S_2FeClFe(CO)Cp^*][PF_6]$ (2)

Under CO, a solution of $[N_2S_2FeClFe(MeCN)Cp^*][PF_6]$ (1) (100 mg, 0.15 mmol) in 5 mL CH₂Cl₂ was stirred from -78 °C to room temperature for 6 h, the solution color gradually changed from initial dark green to light green. After removal of the solvent, the residue was washed with Et₂O (3 × 3 mL) to give a green powder **2** (82.4 mg, 0.12 mmol, 84%). Crystals suitable for X-ray diffraction were obtained from a CH₂Cl₂ solution layered with *n*-hexane. Proton resonances in the ¹H NMR spectrum of **2** are difficult to be accurately assigned due to the paramagnetism. μ_{eff} (CD₂Cl₂, Evans method, 25 °C) = 5.84 μ_{B} . IR (KBr, cm⁻¹): 2918, 2873, 1975(ν_{CO}), 1466, 1431, 1381, 876, 841. ESI-HRMS: Calcd. for [**2**–PF₆]⁺ 516.0431; Found 516.0423. Anal. Calcd for

 $C_{19}H_{33}ClF_6Fe_2N_2OPS_2:$ C, 34.49; H, 5.03; N, 4.23. Found: C, 34.72; H, 5.39; N, 3.79.

4.5. Synthesis of $[N_2S_2FeClFe(^tBuNC)Cp^*][PF_6]$ (3)

At room temperature, 1 equiv. of ^tBuNC (16 µL, 0.15 mmol) was added to a stirred solution of [LFeClFe(MeCN)Cp*][PF₆] (100 mg, 0.15 mmol) in 5 mL CH₃CN. The solution was vigorously stirred for 2 h, whose color immediately changed from initial dark green to yellow. Solvent was removed in *vacuo*, and the crude product was washed with Et₂O (3 × 3 mL) to give a brown powder **3** (78.5 mg, 0.11 mmol, 73%). Crystals suitable for X-ray diffraction were obtained from a CH₂Cl₂ solution layered with *n*-hexane. Proton resonances in the ¹H NMR spectrum of **3** are difficult to be accurately assigned due to its paramagnetism. μ_{eff} (CD₂Cl₂, Evans method, 25 °C) = 5.98 $\mu_{\rm B}$. IR (KBr, cm⁻¹): 2916, 2869, 2137($\nu_{\rm NC}$), 1465, 1376, 1190, 840, 557. ESI-HRMS: Calcd. for [**3**–PF₆]⁺ 571.1208; Found 571.1213. Anal. Calcd for C₂₃H₄₂ClF₆Fe₂N₃PS₂: C, 38.54; H, 5.91; N, 5.86. Found: C, 38.57; H, 6.11; N, 6.36.

4.6. General procedure for catalytic reduction of hydrazine

A CH₃CN (5 mL) solution of 1 (16.8 mg, 0.025 mmol) was placed to a 25 mL Schlenk flask. Then N₂H₄ (16 μ L, 0.50 mmol) was introduced into the stirred solution. After being stirred for 12 h at room temperature, the reaction volatiles were transferred under reduced pressure into a frozen ethereal solution of HCl (4 M, 2 mL) in a 25 mL Schlenk flask. After thawing, the solution was stirred at room temperature for 15 min. All solvents and excess HCl were removed *in vacuo* to yield colorless solids. ¹H NMR analysis (DMSO-d₆) of the resulting colorless solids indicated the presence of NH₄Cl. The NH₄Cl was quantified by integration of the NH₄⁺ resonance with respect to an internal reference of ferrocene. The yields of N₂ were determined by GC.

CRediT authorship contribution statement

Linan Su: Methodology, Validation, Formal analysis, Investigation, Writing - original draft. Dawei Yang: Conceptualization, Formal analysis, Investigation, Writing - review & editing. Baomin Wang: Writing - review & editing. Jingping Qu: Conceptualization, Formal analysis, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

CCDC 1449150, 1955005 contain the supplementary crystallographic data in CIF format for the structure reported. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1E, UK; fax: (+44) 1223-336-033; or email: deposit@ccdc.cam.ac.uk.

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