

行政院國家科學委員會專題研究計畫 成果報告

以含鐵、錳硝基化合物為一氧化氮供給劑及其催化一氧化
氮轉換之研究(2/2)
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中華民國 97 年 10 月 29 日

行政院國家科學委員會補助專題研究計畫 成果報告
 期中進度報告

含鐵、錳硝基化合物之合成及反應性探討及其做為一氧化氮供給劑與催化一氧

化氮轉換之研究

(Synthesis and Reactivity of Fe-/Mn-containing Nitrosyl Complexes: Relevance
to the NO-donor and NO Disproportionation Chemistry)

計畫類別： 個別型計畫 整合型計畫

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計畫參與人員：洪士軒, 林祖涵, 許舒涵, 朱田次瑋

成果報告類型(依經費核定清單規定繳交)： 精簡報告 完整報告

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執行單位：中山醫學大學應用化學系

中華民國 97 年 10 月 30 日

Abstract

The ligand (HS,Se-C₆H₃-4-Me)₂ (**1**) has been synthesized according to the Martin and Figuly procedure and reaction of [Fe(CO)₃(NO)]⁻ with the ligands **1** yielded the desired {Fe(NO)}⁶ [(NO)Fe(S,Se-C₆H₃-4-Me)₂]⁻ (**2**). Reduction of complex **2** with [SPh]⁻ afforded the {Fe(NO)}⁷ [(NO)Fe(S,Se-C₆H₃-4-Me)₂]²⁻ (**3**). In addition, the diiron thiolate nitrosyl complex [(NO)Fe(μ -S,Se-C₆H₃-4-Me)₂Fe(NO)₂]⁻ (**4**) was synthesized by treating complex **2** with Fe(CO)₂(NO)₂. Further reaction of complex **4** with [S,S-CNMe₂]⁻ resulted in another {Fe(NO)}⁷ [(NO)Fe(S,Se-C₆H₃CH₃)(S,S-CNMe₂)]⁻ (**5**). The structures of the all complexes have been characterized by single crystal X-ray diffraction. Complexes **2**, **3**, and **5** show a five coordinated distorted pyramidal geometry and the nitrosyl ligand occupied the axial position with the Fe-N-O bond angle of 177.5(5)° for complex **2**, 170.7(7)° for complex **3**, and 158.4(7)° for complex **5**. In contrast to the distorted square pyramidal complex **2** with a S₄ base and an apical NO group, the geometry of one iron of complex **4** is trigonal bipyramidal ([Fe(NO)(S,Se)₂] core) with a NO ligand occupying the equatorial position. In addition to the structural characterization, the further study on the reactivity and physical characterization of these complexes will be undergoing.

中文摘要

由於一氧化氮在人體的許多生理及病理方面扮演相當重要的角色，這些重要性直接引起許多研究者再度對一氧化氮化學的濃厚興趣，其中亦包含了一氧化氮跟金屬作用產生的金屬硝基化合物。到目前為止一氧化氮確定在人體內扮演的角色包含了對血管舒張收縮的調節、中樞及周遭神經系統的傳導，以及對病原體的免疫。既然一氧化氮扮演了這許多的角色，當人體內的一氧化氮生成或代謝出現問題時就會導致人體的生病，例如高血壓、糖尿病、關節炎以及癲癇等等。因為金屬硝基化合物也經常出現在生物系統內，因此產生利用金屬硝基化合物來調節生物體內一氧化氮濃度的想法。

目前利用 $(\text{HS},\text{Se}-\text{C}_6\text{H}_3-4-\text{Me})_2$ (**1**)與 $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ 進行一連串的反應已合成出一個 $\{\text{Fe}(\text{NO})\}^6$ $[(\text{NO})\text{Fe}(\text{S},\text{Se}-\text{C}_6\text{H}_3-4-\text{Me})_2]^-$ (**2**)，兩個 $\{\text{Fe}(\text{NO})\}^7$ 化合物 $[(\text{NO})\text{Fe}(\text{S},\text{Se}-\text{C}_6\text{H}_3-4-\text{Me})_2]^{2-}$ (**3**)及 $[(\text{NO})\text{Fe}(\text{S},\text{Se}-\text{C}_6\text{H}_3\text{CH}_3)(\text{S},\text{S}-\text{CNMe}_2)]^-$ (**5**)。另外還合成了一個雙鐵原子中心三亞硝基化合物 $[(\text{NO})\text{Fe}(\mu-\text{S},\text{Se}-\text{C}_6\text{H}_3-4-\text{Me})_2\text{Fe}(\text{NO})_2]^-$ (**4**)。接下來將對於這些化合物的電子結構、反應性及對光照的敏感性做一系列的探討。

Synthesis and Reactivity of Fe-/Mn-containing Nitrosyl Complexes: Relevance to the NO-donor and NO Disproportionation Chemistry

1. Introduction

Nitric oxide (NO) which was first characterized by Joseph Priestley in 1772¹ is the simplest thermally paramagnetic molecule and its physical and chemical properties inspire chemists' curiosity continuously. Nitric oxide resulting from automobile engines and industrial power plants had been thought for a long time as an unpleasant, toxic gas and air pollutant, because nitric oxide and its derivatives NO_x can consume ozone O₃ and lead to smog and acid rain similarly to SO₂.² However, in the recent two decades the physiological and biological functions of nitric oxide in living organisms are an area of intense investigation, because more and more function of nitric oxide have been discovered including principal neurotransmitter mediating erectile function,³ a critical endogenous regulator of blood flow and thrombosis,⁴ a major path physiological mediator of inflammation and host defense.⁵ A range of physiological roles of nitric oxide led *Science* to designate nitric oxide (NO) as Molecule of the Year in 1992.⁶

Under the physiological condition, living organisms can regulate the proper concentration of NO by endogenously physiological NO carriers or NO donors in which nitrosyl iron-porphyrin complexes, S-nitrosothiol (RSNO) and dinitrosyl iron complexes (DNICs) are included to promote the regular biological activities. But under the pathophysiological situation, NO overproduction or deficiency can be regulated by delivery within a biological environment of respective metal complexes which are able to bind (NO scavengers) or release nitric oxide (NO donors).⁷ All nitrogen-oxygen-bonded compounds have the potential to produce reactive nitrogen species via decomposition, oxidation or reduction.⁸ In recent years, the potential of iron-sulfur cluster nitrosyls and other metal nitrosyl compounds (M-NO, M = Ru, Cr, Mo, etc.) serving as NO donors have taken on added significance because of their potential use in photodynamic therapy (PDT) for cancer.

Recently, Mascharak et al. published many light-sensitive nitrosyl complexes which had the potential as NO donors including iron,⁹ ruthenium¹⁰ and manganese nitrosyl complexes.¹¹ In contrast to ruthenium nitrosyl complex which releases NO under high-intensity light in the near UV region (340-440 nm),¹⁰ three photolabile {Fe-NO}⁶ nitrosyl complexes, namely [(PaPy₃)Fe(NO)](ClO₄)₂ (PaPy₃H = *N,N*-bis-(2-pyridylmethyl)amine-*N*-ethyl-2-pyridine-2-carboxamide), [(PcPy₃)Fe(NO)](ClO₄)₂ (PcPy₃H = *N,N*-bis(2-pyridylmethyl)-amine-*N'*-(2-pyridylmethyl)acetamide), and [(MePcPy₃)Fe(NO)](ClO₄)₂ (MePcPy₃H = *N,N*-bis(2-pyridylmethyl)-amine-*N'*-[1-(2-pyridinyl)ethyl]acetamide), can rapidly release NO upon illumination with visible light. In addition, in the absence of light, the three iron nitrosyl complexes can deliver NO to alkylthiols such as *N*-acetylpenicillamine, *N*-acetylcysteine, 3-mercaptopropionic acid, and glutathione which often act as potential NO storage in biological system.^{9c} Reduction of these {Fe-NO}⁶ nitrosyl complexes affords the corresponding {Fe-NO}⁷ nitrosyl complexes. The combination of spectroscopic and structural data reveals the Fe(II)-NO⁺ and Fe(II)-NO· formulation for the {Fe-NO}⁶ and {Fe-NO}⁷ species, respectively.^{9d,e} Based on the comparisons of reactivity of {Fe-NO}⁶ and {Fe-NO}⁷ species, Mascharak claimed that the photoactive NO donors are the {Fe-NO}⁶ species with Fe(II)-NO⁺ formulation, not the {Fe-NO}⁷ species with Fe(II)-NO· formulation. In contrast, according to the study of {Mn-NO}⁶ nitrosyl [Mn(PaPy₃)(NO)](ClO₄) and {Mn-NO}⁵ nitrosyl [Mn(PaPy₃)(NO)](NO₃)₂, Mascharak presumed that the {Mn-NO}⁶ species with Mn(II)-NO· formulation demonstrated the NO photosensitivity, and not the {Mn-NO}⁵ species with Mn(II)-NO⁺ formulation.¹¹ Besides, the nitrosyl species [Mn(PaPy₃)(NO)](ClO₄) and [Ru(PaPy₃)(NO)](BF₄)₂ have been employed to successfully deliver NO to biological targets such as myoglobin, cytochrome c oxidase and soluble guanylate cyclase under controlled conditions of illumination.¹² The water-soluble {Mn-NO}⁶ nitrosyl [Mn(PaPy₃)(NO)](ClO₄) which can also rapidly release NO upon activation with visible light of low intensity has been applied to act as a

very special and efficient inhibitor of cysteine protease papain that can be conveniently controlled with light.¹³ This manganese nitrosyl complex was also encapsulated a solgel-derived hydride material that had the potential to rapidly generate NO at specific site or transfer NO to biological targets.¹⁴

The purpose of this research is to synthesize iron and manganese nitrosyl complexes with different donor ligands. The further reactivity study and physical characterization of the synthesized iron and manganese nitrosyl complexes will allow us to explore the electronic configuration $\{M(NO)_x\}^n$ of metal nitrosyls easily releasing NO, to elucidate how the different donor ligands inducing and facilitating NO release from metal nitrosyl complex, to investigate which NO bonding mode (NO^+ , $\cdot NO$, or NO^-) immediately catalyzing NO disproportionation when NO react with metal complex.

2. Experimental

Manipulations, reactions, and transfers were conducted under nitrogen according to Schlenk techniques or in a glovebox (nitrogen gas). Solvents were distilled under nitrogen from appropriate drying agents (diethyl ether from CaH_2 ; acetonitrile from $CaH_2-P_2O_5$; methylene chloride from P_2O_5 ; hexane and tetrahydrofuran(THF) from sodium benzophenone) and stored in dried, N_2 -filled flasks over 4Å molecular sieves. Nitrogen was purged through these solvents before use. Solvent was transferred to the reaction vessel via stainless cannula under positive pressure of N_2 . The reagents tetraphenylphosphonium bromide ($[PPh_4][Br]$) (Strem), iron pentacarbonyl (Strem), sodium nitrite (acros), 4-methylbenzenethiol, n-butyllithium, N,N,N',N' -tetramethylethylenediamine, nitrosonium tetrafluoroborate (Aldrich-Sigma) were used as received. $[PPh_4][Fe(CO)_3(NO)]$ has been prepared according to literature procedures. Infrared spectra of the nitrosyl $\nu(NO)$ stretching frequencies were recorded on a Jasco FT/IR-4100 spectrophotometer. Solid samples were examined as KBr discs and solution samples were acquired in a sealed solution cell with KBr windows and 0.1 mm Teflon spacers. UV/vis spectra were recorded on a GBC Cintra 101. 1H NMR spectra were recorded

in a Varian Unity-400 spectrometer in CDCl_3 at room temperature. NMR spectra are referred to the internal residual solvent. Analyses of carbon, hydrogen, and nitrogen were obtained with a CHN analyzer (Heraeus).

Preparation of (HS, Se-C₆H₃-4-Me)₂ (1). A 250-mL Schlenk flask equipped with magnetic spin bar, an addition funnel, and a septum was flame-dried under vacuum, cooled under nitrogen. Dry hexane (50 mL), TMEDA (32 mL, 0.22 mol), and 2.5 M n-butyllithium (88 mL, 0.22 mol) were loaded into the flask by syringe. 4-methylbenzenethiol (12.42 g, 0.1 mol) dissolving in 50 mL hexane was transferred to the addition funnel by cannula under positive N_2 gas at room temperature and the hexane solution of 4-methylbenzenethiol was added drop by drop into the resultant suspension at 0 °C. When the addition was completed, the reaction mixture was stirred at ambient temperature for 24 h to yield off-white solid. Selenium powder (17.36 g, 0.22 mol) was added slowly to this well-stirred suspension and the now gray suspension was stirred for an additional 24 h. The hexane was removed under vacuum and replaced with 125 mL THF. The THF solution was treated at 0 °C with LiAlH_4 (4.4 g, 0.12 mol). After the initial exothermic reaction subsided, the solution was refluxed for 5 h, then cooled to the room temperature, and poured slowly into 2 M HCl (250 mL) at 0 °C. After checking the pH, the acidic solution was extracted with diethyl ether (3 × 200 mL). The diethyl ether was dried (MgSO_4) and then exposed to air overnight. When the diethyl ether was evaporated into the oil yellow residue, 60 mL hexane was added to precipitate the yellow solid (HS,Se-C₆H₃-4-Me)₂ (**1**) (yield 10.83g, 53.5%). The orange-yellow crystals suitable for X-ray crystallography were afforded by evaporating the diethyl ether solution of complex **1** slowly for 5 days under nitrogen atmosphere at -15 °C. The ¹H NMR (CDCl_3): δ 2.23 (s) (CH_3), 3.81 (s) (SH), 6.93 (d), 7.24 (d), 7.43 (s) (C_6H_3) ppm . Absorption spectrum (THF) [λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): ?(?). Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{S}_2\text{Se}_2$: C, 41.59; H, 3.49; N, 2.95. Found: C,; H,; N,.

Preparation of [PPh₄][(NO)Fe(S,Se-C₆H₃-4-Me)₂] (2). To a stirred THF solution (30 mL) containing [PPh₄][Fe(CO)₃(NO)] (1.02 g, 2 mmol) and (HS,Se-C₆H₃-4-Me)₂ (**1**) (0.808 g, 2 mmol) was injected 50 mL of air at ambient temperature. After the mixture solution was stirred for 3 days,

the reaction solution was filtered through Celite. The resulting filtrate was concentrated to 5 mL and 30 mL hexane was added to precipitate the dark red solid $[\text{PPh}_4][(\text{NO})\text{Fe}(\text{S},\text{Se}-\text{C}_6\text{H}_3-4\text{-Me})_2]$ (**2**) (1.369 g, 83%). Diffusion of hexane into a CH_2Cl_2 solution of complex **2** at $-15\text{ }^\circ\text{C}$ for four weeks led to red crystals suitable for X-ray crystallography. IR: 1785 vs (ν_{NO}) cm^{-1} (THF); 1781 vs (ν_{NO}) cm^{-1} (KBr). ^1H NMR (CDCl_3): δ 2.21 (s) (CH_3), 6.74 (d), 7.41- 7.48 (m), 7.56 -7.61 (m), 7.70-7.74 (m) (C_6H_3) ppm. Absorption spectrum (CH_2Cl_2) [λ_{max} , nm (ϵ , $\text{M}^{-1}\text{ cm}^{-1}$): ?(?), ?(?), ?(?). Anal. Calcd for $\text{C}_{38}\text{H}_{32}\text{FeNOPS}_2\text{Se}_2$: C, 55.15; H, 3.90; N, 1.69. Found: C,; H,; N,.

Preparation of $[\text{PPh}_4]_2[(\text{NO})\text{Fe}(\text{S},\text{Se}-\text{C}_6\text{H}_3-4\text{-Me})_2]$ (3**).** The CH_3CN solution (7 mL) of $[\text{PPh}_4][\text{SPh}]$ (0.225 g, 0.5 mmol) was added slowly to the Schlenk tube (20 mL) containing CH_3CN solution (8 mL) of complex **2** (0.414 g, 0.5 mmol) by cannula under positive N_2 pressure without stirring at ambient temperature. After the reaction solution was stored without stirring overnight at $0\text{ }^\circ\text{C}$ under N_2 atmosphere, the upper CH_3CN solution was removed under a positive pressure of N_2 and the residual dark-brown crystals was washed twice by CH_3CN . The dark-brown crystals suitable for X-ray crystallography was then dried under N_2 purge to afford the product $[\text{PPN}]_2[(\text{NO})\text{Fe}(\text{S},\text{Se}-\text{C}_6\text{H}_3-4\text{-Me})_2]$ (**3**) (0.384 g, 65.8%). IR: 1629 vs (ν_{NO}) cm^{-1} (KBr). Absorption spectrum (CH_2Cl_2) [λ_{max} , nm (ϵ , $\text{M}^{-1}\text{ cm}^{-1}$): ?(?), ?(?), ?(?). Anal. Calcd for $\text{C}_{62}\text{H}_{52}\text{FeNOP}_2\text{S}_2\text{Se}_2$: C, 63.81; H, 4.49; N, 1.20. Found: C,; H,; N,.

Preparation of $[\text{PPh}_4][(\text{NO})\text{Fe}(\mu\text{-S},\text{Se}-\text{C}_6\text{H}_3-4\text{-Me})_2\text{Fe}(\text{NO})_2]$ (4**).** To a Schlenk tube containing complex **2** (0.248 g, 0.3 mmol) was added the THF solution (6 mL) of $\text{Fe}(\text{CO})_2(\text{NO})_2$ (0.3 mmol) freshly prepared (obtained from reaction of $[\text{NO}][\text{BF}_4]$ and $[\text{PPh}_4][\text{Fe}(\text{CO})_3(\text{NO})]$ in THF in a 1:1 ratio) by cannula under a positive pressure of N_2 at ambient temperature. The reaction mixture was stirred overnight and then the solution was filtered through Celite. The filtrate was concentrated to 5 mL and 30 mL hexane was added to precipitate the green solid $[\text{PPh}_4][(\text{NO})\text{Fe}(\mu\text{-S},\text{Se}-\text{C}_6\text{H}_3-4\text{-Me})_2\text{Fe}(\text{NO})_2]$ (**4**) (0.252 g, 89%). Diffusion of hexane into a THF solution of complex **4** at $-15\text{ }^\circ\text{C}$ for four weeks led to green crystals suitable for X-ray crystallography. IR: 1761 sh, 1742 s, 1717 m (ν_{NO}) cm^{-1} (THF); 1755 s, 1729 s, 1715 s (ν_{NO}) cm^{-1}

(KBr). ^1H NMR (CDCl_3): δ 2.10, 2.14 (s) (CH_3), 6.63 (d), 7.26- 7.31 (m), 7.57 -7.73 (m), 7.86 (m) (C_6H_3) ppm. Absorption spectrum (CH_2Cl_2) [λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): ?(?), ?(?), ?(?). Anal. Calcd for $\text{C}_{38}\text{H}_{32}\text{Fe}_2\text{N}_3\text{O}_3\text{PS}_2\text{Se}_2$: C, 48.38; H, 3.42; N, 4.45. Found: C,; H,; N,.

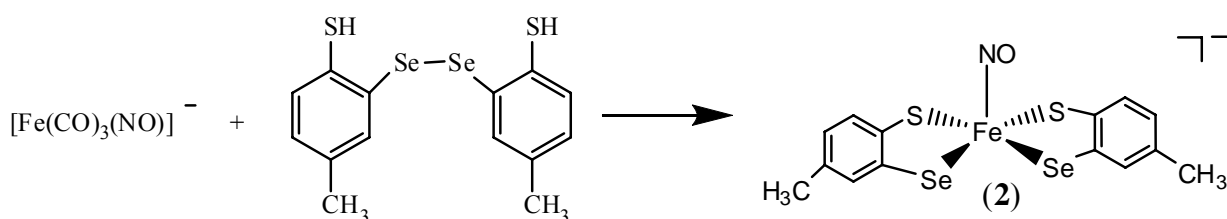
Preparation of $[\text{PPh}_4][(\text{NO})\text{Fe}(\text{S},\text{Se}-\text{C}_6\text{H}_3-4-\text{Me})(\text{S},\text{S}-\text{CNMe}_2)]$ (5). 15 mL THF was added to the Schlenk tube containing complex **4** (0.188 g, 0.2 mmol) and $[\text{PPh}_4][\text{S},\text{S}-\text{CNMe}_2]$ (0.180 g, 0.4 mmol) by cannula under a positive pressure of N_2 at ambient temperature. The reaction mixture was stirred for 5 days and then the reaction Schlenk tube was stood to precipitate the yellow-green solid. The upper green solution was discarded by cannula under positive N_2 pressure and the residual yellow-green solid was washed twice with 10 mL THF. The yellow-green solid was dried under vacuum and redissolved in CH_3CN -THF (2:1 volume ratio) solution. Diffusion of diethyl ether into the CH_3CN -THF solution at $-15\text{ }^\circ\text{C}$ for two weeks led to green crystals of $[\text{PPh}_4][(\text{NO})\text{Fe}(\text{S},\text{Se}-\text{C}_6\text{H}_3-4-\text{Me})(\text{S},\text{S}-\text{CNMe}_2)]$ (**5**) (0.14g, 46.8%) suitable for X-ray crystallography. IR: 1634 s (ν_{NO}) cm^{-1} (KBr); 1646 s (ν_{NO}) cm^{-1} (CH_3CN). Absorption spectrum (THF) [λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): ?(?), ?(?) ()]. Anal. Calcd for $\text{C}_{34}\text{H}_{32}\text{FeN}_2\text{OPS}_3\text{Se}$: C, 54.70; H, 4.32; N, 3.75. Found: C,; H,; N,.

3. Results and discussion

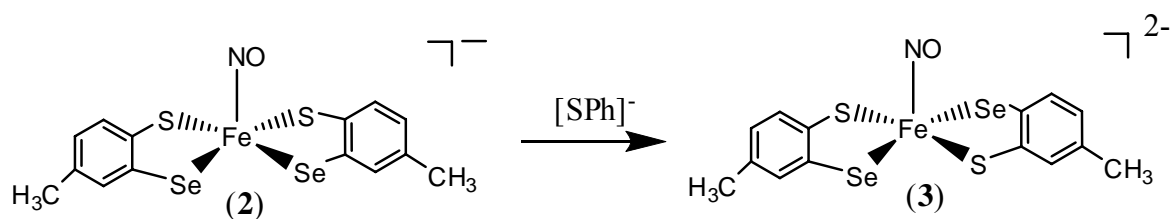
Preparation and characterization of $[\text{PPh}_4][(\text{NO})\text{Fe}(\text{S},\text{Se}-\text{C}_6\text{H}_3-4-\text{Me})_2]$ (2)
 $[\text{PPh}_4]_2[(\text{NO})\text{Fe}(\text{S},\text{Se}-\text{C}_6\text{H}_3-4-\text{Me})_2]$ (3). The five-coordinated $[\text{PPh}_4][(\text{NO})\text{Fe}(\text{S},\text{Se}-\text{C}_6\text{H}_3-4-\text{Me})_2]$ (**2**), isolated as a thermally stable, dark red-brown solid after recrystallization from THF/hexane, was prepared by treatment of THF solution of $[\text{PPh}_4][\text{Fe}(\text{CO})_3(\text{NO})]$ with 1 equiv of $(\text{HS},\text{Se}-\text{C}_6\text{H}_3-4-\text{Me})_2$ at ambient temperature for 3 days (Scheme 1). Complex **2** is soluble in CH_2Cl_2 , THF and CH_3CN . The chemical shift, δ 2.21(s) (CH_3), 6.74 (d) (C_6H_3) ppm (CDCl_3), assigned for the protons of the $[\text{S}, \text{Se}-\text{C}_6\text{H}_3-4-\text{Me}]^{2-}$ ligands, indicated that complex **2** is a diamagnetic species. The infrared spectrum of complex **2** shows one sharp stretching band at 1785 cm^{-1} (THF) (1781 cm^{-1} (KBr)) in the $\nu(\text{NO})$ region. According to the reported data, the electronic

structure of the $\{\text{Fe}(\text{NO})\}^6$ core ($S = 0$) of complex **2** is best described as NO^+ coordinating to a d^6 low-spin Fe^{II} ($S = 0$). Further reaction of complex **2** with 1 equiv $[\text{SPh}]^-$ in CH_3CN at ambient temperature overnight afforded the red-brown crystals (Scheme 2). The red-brown crystals were identified as the five-coordinated $[\text{PPh}_4]_2[(\text{NO})\text{Fe}(\text{S},\text{Se}-\text{C}_6\text{H}_3-4\text{-Me})_2]$ (**3**) by UV-vis/ IR spectra, and X-ray diffraction studies. Complex **3** is thermal stable, air sensitive, and insoluble in CH_3CN . Instead of the direct nucleophilic attack of $[\text{SR}]^-$ on the coordinated NO^+ yielding RSNO and $[\text{Fe}(\text{S},\text{Se}-\text{C}_6\text{H}_3-4\text{-Me})_2]^{2-}$, the formation of complex **3** indicated that $[\text{SR}]^-$ reduced the $\{\text{Fe}(\text{NO})\}^6$ core of complex **2** to the $\{\text{Fe}(\text{NO})\}^7$ core of complex **3**, accompanied by byproduct of $(\text{PhS})_2$ identified by ^1H NMR. The lower energy $\nu(\text{NO})$ band of complex **3** at 1629 cm^{-1} (KBr) which fall into the range ($1620 - 1675\text{ cm}^{-1}$) observed for five-coordinated iron-nitrosyl complexes having the $\{\text{Fe}(\text{NO})\}^7$ configuration with an $S = 1/2$ ground state and shift by $\sim 150\text{ cm}^{-1}$ from that of complex **2** also implicate the reduction process occurred in complex **2**. The effective magnetic moment in solid state by SQUID magnetometer was $1.66\ \mu_{\text{B}}$ for complex **3** which is consistent with a paramagnetic form. Based on these studies, the electronic structure of $\{\text{Fe}(\text{NO})\}^7$ core is best described as a low-spin d^6 $\text{Fe}(\text{II})$ ($S = 0$) coordinated by $\text{NO}\cdot$ radical ($S = 1/2$) to produce the total spin state of $S = 1/2$, i.e., the $\{\text{Fe}(\text{NO})\}^7$ **3** having a low-spin d^6 $\text{Fe}(\text{II})\text{-NO}\cdot$ radical configuration in a distorted square pyramidal ligand field. Although the intermediate spin $\text{Fe}(\text{III})$ ($S = 3/2$) coupled to coordinated triplet NO^- ($S = 1$) can not be unambiguously ruled out.

Scheme 1



Scheme 2



Molecular structures of complexes 2 and 3. Figure 1 shows a five coordinated distorted rectangular pyramidal geometry. The nitrosyl ligand occupied the axial position in a nearly linear mode with the Fe-N(1)-O(1) bond angle of $177.5(5)^\circ$ and two terminal thiolates and two terminal selenolates located the equatorial positions with $N(1)-Fe-S(1) = 100.67(1)$, $N(1)-Fe-S(2) = 108.34(17)$, $N(1)-Fe-Se(1) = 102.90(17)$, and $N(1)-Fe-Se(2) = 101.00(16)^\circ$. The Fe-N(1) distance of $1.602(4)$ Å in complex **2** is significantly shorter than those of $\{Fe(NO)\}^7 [Fe(NO)(S_2CNMe_2)_2]$ (Fe-N = $1.705(16)$ Å), $\{Fe(NO)\}^8 [Fe(NO)(S_2C_2O_2)_2]^{2-}$ (Fe-N = $1.690(2)$ Å), and the NO-inactivated form Fe-NHase (Fe-N(O) = 1.65 Å). The short Fe-N(O) distance and almost linear Fe-N-O angle of complex **2** are typical characters of $\{Fe-NO\}^6$ nitrosyls. Besides, the strong π -donating ability of the bidentate $[S,Se-C_6H_3-4-Me]^{2-}$ ligands may contribute to the shorter Fe-S bond distance of $2.235(14)$ Å (average) in complex **2**, compared with those of $[Fe(NO)(S_2CNMe_2)_2]$ ($2.294(2)$ Å) and the NO-inactivated form Fe-NHase (2.32 Å). This phenomenon that the iron atom lies 0.523 Å above the mean plane defined by the two sulfur atoms and two selenium atoms plane toward the axial nitrosyl ligand, was also observed in the other rectangular-based pyramidal iron-nitrosyl compounds. The ORTEP diagram of the anionic complex **3** (Figure 2) shows a distorted rectangular pyramidal geometry with the Fe-N(1)-O(1) bond angle of $170.7(7)^\circ$. The Fe-N(1)-O(1) bond angle of $170.7(7)^\circ$ and the Fe-N bond distance of $1.686(8)$ Å in complex **3**, consistent with the typical $\{Fe-NO\}^7$ nitrosyls, indicated that the thiolate ligand reduced the $\{Fe-NO\}^6$ core complex **2** to the $\{Fe-NO\}^7$ core complex **3**. The N(1)-O(1) distance of complex **3** ($1.138(10)$ Å) is comparable to the N-O distance of free NO (1.15 Å) but far from the N-O distance

of NO⁻ (1.26 Å). The Fe-N(1)-O(1) bond angle and the N(1)-O(1) distance in complex **3** revealed that the nitrosyl ligand is coordinated to iron atom in a NO radical mode. Similarly, the iron atom lies 0.571 Å above the mean plane defined by the two sulfur atoms and two selenium atoms plane toward the axial nitrosyl ligand.

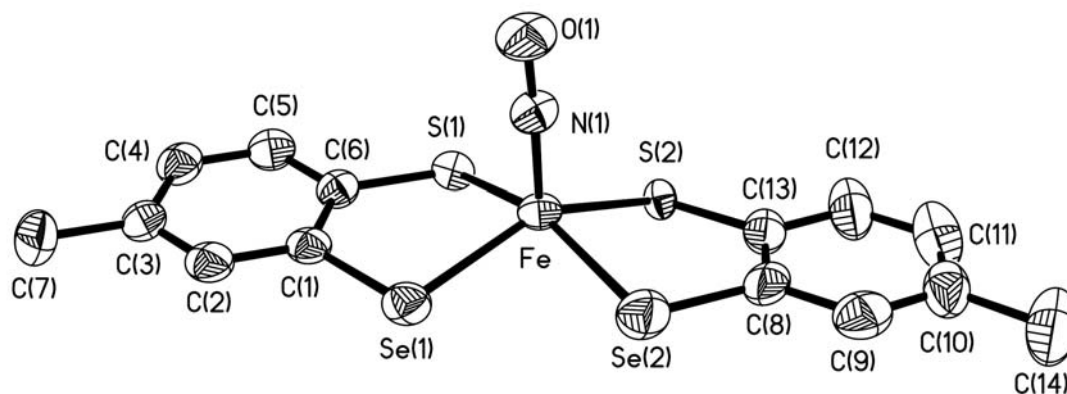


Figure 1. ORTEP drawing and labeling scheme of [(NO)Fe(S,Se-C₆H₃-4-Me)₂]⁻ (**2**) anion with thermal ellipsoids drawn at 50 % probability level.

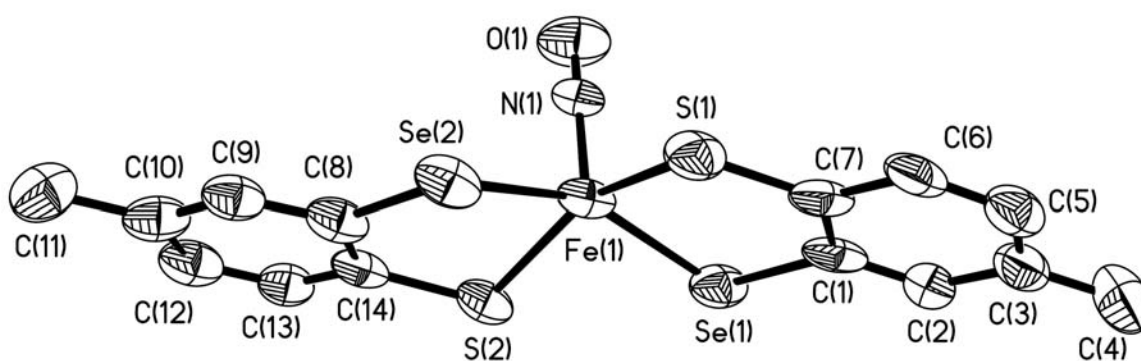
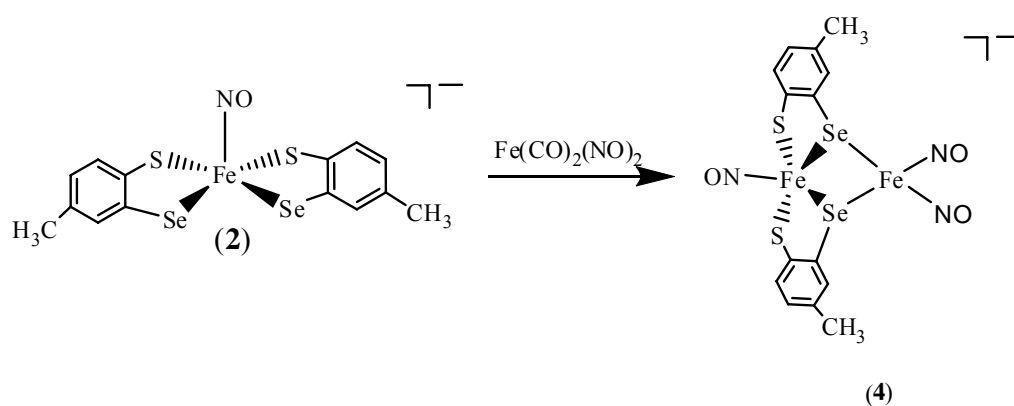


Figure 2. ORTEP drawing and labeling scheme of [(NO)Fe(S,Se-C₆H₃-4-Me)₂]²⁻ (**3**) anion with thermal ellipsoids drawn at 50 % probability level.

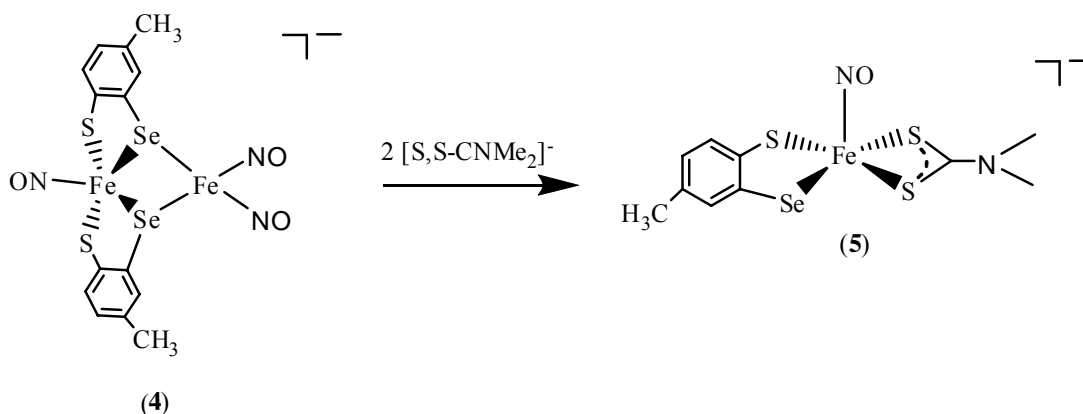
Preparation and characterization of [PPh₄][(NO)Fe(μ -S,Se-C₆H₃-4-Me)₂Fe(NO)₂] (4**) and [PPh₄][(NO)Fe(S,Se-C₆H₃-4-Me)(S,S-CNMe₂)] (**5**).** As shown in Scheme 3, diiron selenolate thiolate nitrosyl complex [PPh₄][(NO)Fe(μ -S,Se-C₆H₃-4-Me)₂Fe(NO)₂] (**4**) was synthesized in a

single step by treating $\text{Fe}(\text{CO})_2(\text{NO})_2$ with complex **2** in THF under a N_2 atmosphere at ambient temperature. Complex **4**, soluble in THF, CH_2Cl_2 , and CH_3CN , was isolated as a dark green solid. The IR spectrum of complex **4** in the aprotic solvent THF reveals three $\nu(\text{NO})$ absorption bands at 1761 sh, 1742 s, and 1717 m cm^{-1} . Complex **4** exhibits a diagnostic ^1H NMR spectrum with resonances at 2.10, 2.14 (s) (CH_3), 6.63 (d) (C_6H_3) ppm (CDCl_3). On the basis of ^1H NMR, EPR, and magnetic measurements, complex **4** is characterized as a diamagnetic species. Further reaction of complex **4** with 2 equiv $[\text{S,S-CNMe}_2]^-$ in THF at ambient temperature for 5 days afforded the green solids (Scheme 4). The green solids were identified as the five-coordinated $[\text{PPh}_4][(\text{NO})\text{Fe}(\text{S,Se-C}_6\text{H}_3\text{-4-Me})(\text{S,S-CNMe}_2)]$ (**5**) by UV-vis/ IR spectra, and X-ray diffraction studies. Complex **5** is thermal stable, air sensitive, and soluble in CH_3CN . The lower energy $\nu(\text{NO})$ band of complex **3** at 1633 cm^{-1} (KBr) which fall into the range ($1620 - 1675 \text{ cm}^{-1}$) observed for five-coordinated iron-nitrosyl complexes having the $\{\text{Fe}(\text{NO})\}^7$ configuration with an $S = 1/2$ ground state. The effective magnetic moment in solid state by SQUID magnetometer was $1.60 \mu_{\text{B}}$ for complex **5** which is consistent with a paramagnetic form. Based on these studies, the electronic structure of $\{\text{Fe}(\text{NO})\}^7$ core is best described as a low-spin d^6 Fe(II) ($S = 0$) coordinated by NO^\cdot radical ($S = 1/2$) to produce the total spin state of $S = 1/2$, i.e., the $\{\text{Fe}(\text{NO})\}^7$ **5** having a low-spin d^6 Fe(II)- NO^\cdot radical configuration in a distorted square pyramidal ligand field.⁸² Although the intermediate spin Fe(III) ($S = 3/2$) coupled to coordinated triplet NO^- ($S = 1$) can not be unambiguously ruled out.

Scheme 3



Scheme 4



Molecular structure of complex 5. The ORTEP diagram of the anionic complex **5** (Figure 3) shows a distorted rectangular pyramidal geometry similar to that of complex **2**, with the Fe-N(1)-O(1) bond angle of $158.4(7)^\circ$ that is close to the corresponding angle (158.6°) in the NO-inactivated Fe-NHase. The Fe-N(1)-O(1) bond angle of $158.4(7)^\circ$ and the Fe-N bond distance of $1.660(8) \text{ \AA}$ in complex **5** are consistent with the typical $\{\text{Fe-NO}\}^7$ core nitrosyls. The N(1)-O(1) distance of complex **5** ($1.170(8) \text{ \AA}$) is comparable to the N-O distance of free NO (1.15 \AA) but far from the N-O distance of NO^- (1.26 \AA). The Fe-N(1)-O(1) bond angle and the N(1)-O(1) distance in complex **5** revealed that the nitrosyl ligand is coordinated to iron atom in a NO radical mode. Similarly, the iron atom lies 0.604 \AA above the mean plane defined by the four sulfur atoms plane toward the axial nitrosyl ligand.

4. Conclusions

The $\{\text{Fe(NO)}\}^6$ core $[\text{PPh}_4][(\text{NO})\text{Fe}(\text{S},\text{Se}-\text{C}_6\text{H}_3-4-\text{Me})_2]$ (**2**), two $\{\text{Fe(NO)}\}^7$ core $[\text{PPh}_4]_2[(\text{NO})\text{Fe}(\text{S},\text{Se}-\text{C}_6\text{H}_3-4-\text{Me})_2]$ (**3**), $[\text{PPh}_4][(\text{NO})\text{Fe}(\text{S},\text{Se}-\text{C}_6\text{H}_3-4-\text{Me})(\text{S},\text{S}-\text{CNMe}_2)]$ (**5**) and diiron chalcogenolate nitrosyl complex $[\text{PPh}_4][(\text{NO})\text{Fe}(\mu\text{-S},\text{Se}-\text{C}_6\text{H}_3-4-\text{Me})_2\text{Fe}(\text{NO})_2]$ (**4**) have been synthesized successfully and characterized by IR, UV/vis, ^1H NMR, and SQUID. Studies on the iron chalcogenolate nitrosyl complexes allow more understanding of geometrical structures, electronic properties, and reactivity patterns of nitrosyl complexes

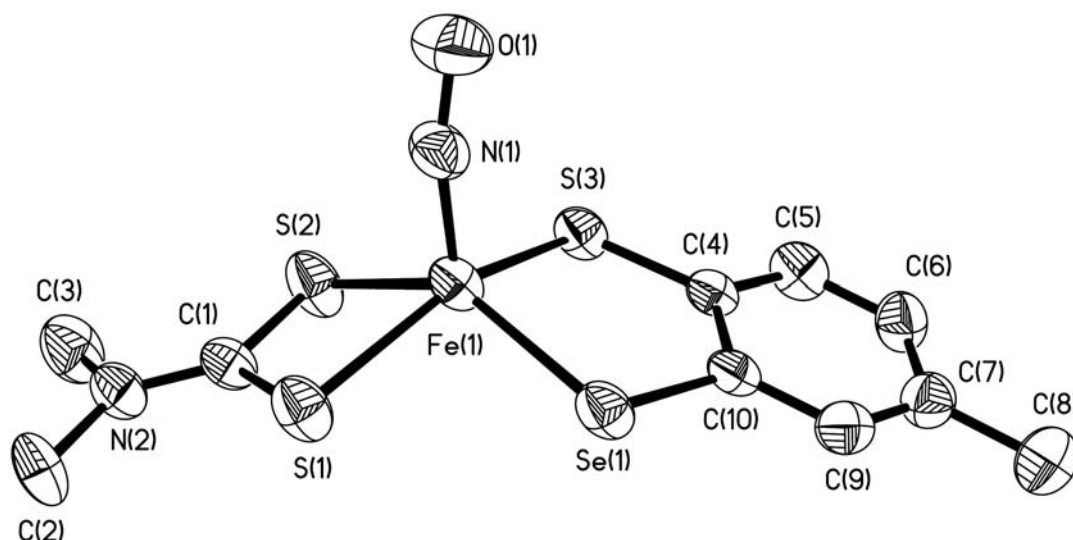


Figure 3. ORTEP drawing and labeling scheme of $[(\text{NO})\text{Fe}(\text{S},\text{Se}-\text{C}_6\text{H}_3-4\text{-Me})(\text{S},\text{S}-\text{CNMe}_2)]^-$ (**5**) anion with thermal ellipsoids drawn at 50 % probability level.

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