A New Hexanuclear Iron–Selenium Nitrosyl Cluster: Primary Exploration of the Preparation Methods, Structure, and Spectroscopic and Electrochemical Properties

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A new hexanuclear iron–selenium nitrosyl cluster, [(n-Bu)$_4$N]$_2$[Fe$_6$Se$_6$(NO)$_6$]$_2$ (1), and a hexanuclear iron–sulfur nitrosyl cluster, [(n-Bu)$_4$N]$_2$[Fe$_6$S$_6$(NO)$_6$] (2), were synthesized by the solvent-thermal reactions of [(n-Bu)$_4$N][Fe(CO)$_3$NO] with selenium or sulfur in methanol, while a tetraneuclear iron–sulfur nitrosyl cluster, (Me$_4$N)[Fe$_4$S$_4$(NO)$_4$] (3), was also prepared by the solvent-thermal reaction of FeCl$_2$·4H$_2$O with thiourea in the presence of (CH$_3$)$_2$NCl, NaNO$_2$, and methanol. Complexes 1–3 were characterized by IR, UV−vis, $^1$H NMR, electrochemistry, and single-crystal X-ray diffraction analysis. IR spectra of complexes 1 and 2 show the characteristic NO stretching frequencies at 1694 and 1698 cm$^{-1}$, respectively, while the absorptions of complex 3 appear at 1799, 1744, and 1710 cm$^{-1}$. The UV−vis spectra of complexes 1–3 show different bands in the range of 259–562 nm, which are assigned to the transitions between orbitals delocalized over the Fe−S cluster, the ligand-to-metal charge transfer, $\pi^*$NO−d$_{Fe}$, and the metal-to-ligand charge transfer, d$_{Fe}$−$\pi^*$NO. Single-crystal X-ray structural analysis reveals that complex 1 crystallizes in the monoclinic P2(1)/n space group with two molecules per unit cell. Two parallel “chair-shaped” structures, consisting of three iron and three selenium atoms, are connected by Fe−Se bonds with an average distance of 2.341 Å; each iron center is bonded to three selenium atoms and a nitrogen atom from the nitrosyl ligand with a pseudotetrahedral center geometry. Cyclic voltammograms of complexes 1 and 2 display two cathodic and three anodic current peaks with an unusually strong cathodic peak. Further electrochemical investigations demonstrated that the intensity of the unusually strong peak is a result of at least three processes. One is the quasi-reversible reduction, and the other two are from an irreversible electrochemical process, in which the compound goes through a typical electron transfer and chemical reaction mechanism. Compound 3 shows three quasi-reversible reductions.

Introduction

Several decades ago, scientists demonstrated that some iron−sulfur clusters were present at the active sites of a large number of enzymes and electron-transfer proteins; for instance, the cubane-like [Fe$_4$S$_4$] cluster was found in ferredoxins and the cuboidal subunit was found in iron−sulfur nitrosyl clusters, such as [Fe$_4$S$_3$(NO)$_7$]$^-$, and in Roussin’s black salt anion [Fe$_4$S$_3$(NO)$_7$]$^-$.[4] The latter is the most common iron−sulfur nitrosyl cluster, and its preparation methods, structure, and spectroscopic and electrochemical properties have been studied extensively.[5] Herein, we report the synthesis and characterization of two new hexanuclear iron−sulfur nitrosyl clusters, [Fe$_6$S$_6$(NO)$_6$] ($X = S$-Me, S-Et, S-CH$_2$Ph, S-CH$_2$C$_6$H$_11$, Cl, Br),[6] and the synthesis and characterization of a novel tetraneuclear iron−sulfur nitrosyl cluster, [Fe$_4$S$_4$(NO)$_4$] (X = Cl, Br, I),[7] which are potentially important for understanding the electron transfer and chemical reaction mechanism of the iron−sulfur nitrosyl cluster.
[Fe₅S₅(NO)₄]₄⁺−, and [Fe₅S₆(NO)]₂−−⁷ were also obtained. Recently, because the important functions of nitric oxide (NO) in diverse physiological processes have been gradually recognized by researchers,5,6 some of which include controlling the blood pressure, regulating gene transcription, inhibiting tumor growth, modulating vasodilation, smoothing muscle proliferation, and acting as biological messengers, these iron−sulfur nitrosyl clusters caught people’s attention once more as potential physiological NO donors.7 However, some clusters, such as [Fe₅S₅(NO)₄]⁺, were obtained only by complicated multistep procedures.8 Subsequently, a new [Fe₅S₅(NO)]₄⁻ cluster was synthesized with an improved one-step synthetic method, in which [Fe₅S₅(NO)]⁺ was used as one of the starting materials.9 Yet, despite many known examples of iron−sulfur nitrosyl clusters, iron−selenium nitrosyl clusters are extremely rare. To date, only one iron−selenium nitrosyl cluster, [Ph₄As][Fe₅Se₅(NO)₃], has been reported, with no characterization other than its structure.10 Interestingly, Surerus and co-workers11 demonstrated through Mössbauer and electron paramagnetic resonance (EPR) spectra that the cluster binding site of beef heart aconitase was found to have higher catalytic activity than the native sulfur-containing enzyme when isocitrate was used as the substrate.12 Our work focuses on the synthesis of iron nitrosyl compounds containing a polynuclear framework, and we have reported a cyclic tetranuclear cluster, [Fe(NO)(imidazolate)]₄, and several dinuclear iron compounds, [Fe₂((µ-RR)²(NO)₄])₃ (R = n−Pr, t−Bu, 6−methyl−2−pyridyl, and 4,6−dimethyl−2−pyrimidyl).13 Here we report the syntheses, characterizations, and structures of a new hexanuclear iron−selenium nitrosyl cluster, [(n−Bu)₄N][Fe₅Se₅(NO)]₄] (1), a hexanuclear iron−sulfur nitrosyl cluster, [(n−Bu)₄N][Fe₅S₅(NO)]₄] (2), and a tetranuclear iron−sulfur nitrosyl cluster, (Me₂N)₃[Fe₄S₄(NO)]⁻ (3). The syntheses and investigations of these complexes help us gain insight on the structures of iron nitrosyl clusters and establish the important relationship between the structures and functions of these molecules.

Experimental Section

Materials and Methods. [(n−Bu)₄N][Fe(NO)(CO)] was synthesized according to the reported procedure but with substitution of (n−Bu)₄NCl for (n−Bu)₄NBr.14 Other chemicals were purchased from Aldrich Chemical Co. and were used without further purification. All solvents were purified and/or dried by standard techniques and degassed under vacuum prior to use, and all experiments were conducted under a nitrogen atmosphere without a special description. IR spectra were recorded on a Nicolet AVATAR 370 FTIR spectrophotometer. UV−vis spectra were measured on a Varian Cary 350 Bio UV−vis spectrophotometer. The ¹H NMR spectra were obtained on a Bruker 400 MHz NMR spectrometer, using acetonitrile−d₃ as the solvent and tetramethylsilane as the internal standard.

Synthesis of [(n−Bu)₄N][Fe₅Se₅(NO)]₄] (1). [(n−Bu)₄N][Fe−CO(NO)] (103 mg, 0.25 mmol), selenium (79 mg, 1 mmol), and methanol (4 mL) were mixed in a vial under a nitrogen atmosphere. The vessel was then sealed and heated at 85°C for 48 h. The autoclave was subsequently allowed to cool to room temperature. After the reaction solution was filtered and washed using methanol, a black solid was obtained. The black solid was then dissolved in acetonitrile, and diethyl ether was slowly added to the solution. The mixed solution was placed in a glovebox at −35°C overnight to crystallize. The black crystals, suitable for X−ray crystallography, were collected by filtration, washed with methanol, and dried under vacuum for several hours. Yield: 52 mg (85%, based on [(n−Bu)₄N][Fe(NO)(CO)]). FTIR: ν(KBr) 1694 (CH₃CN), 1683 (KBr) cm⁻¹. UV−vis spectrum: 259, 297 nm (CH₃CN). ¹H NMR (CD₃CN, ppm): 3.06 (t, 8H), 1.58 (m, 8H), 1.33 (m, 8H), 0.95 (t, 12H).

Synthesis of [(n−Bu)₄N][Fe₅Se₅(NO)]₄] (2). Compound 2 was obtained using sulfur (32 mg, 1 mmol) by the same procedure at 120°C as that described above for 1. Yield: 46 mg (92%, based on [(n−Bu)₄N][Fe(NO)(CO)]). FTIR: ν(KBr) 1698 (CH₃CN), 1678 (KBr) cm⁻¹. UV−vis spectrum: 288 nm (CH₃CN). ¹H NMR (CD₃CN, ppm): 3.06 (t, 8H), 1.58 (m, 8H), 1.33 (m, 8H), 0.95 (t, 12H).

Synthesis of (Me₂N)₃[Fe₄S₄(NO)]⁻ (3). FeCl₃·4H₂O (97.3 mg), thiourea (116.2 mg), (CH₃)₄NCl (57.5 mg), NaNO₂ (108.8 mg), and methanol (3 mL) were mixed in a vial under a nitrogen atmosphere. The vessel was sealed and heated at 85°C for 48 h. The autoclave was then allowed to cool to room temperature. The solution was filtered and washed using methanol, and the solid mixture was dissolved in acetonitrile and filtered to remove the undissolved white solid. Subsequently, diethyl ether was slowly added to the solution, and the mixed solution was placed in a glovebox at −35°C overnight to crystallize. The black crystals, suitable for X−ray crystallography, were collected by filtration, washed with methanol, and dried under vacuum for several hours. Yield: 33 mg (88%, based on FeCl₃·4H₂O). FTIR: ν(KBr) 1799, 1744, 1710 (CH₃CN), 1798, 1728, 1712 (KBr) cm⁻¹. UV−vis spectrum: 285, 347, 534, 584 nm (CH₃CN). ¹H NMR (CD₃CN, ppm): 3.05 (t, 8H), 1.58 (m, 8H), 1.33 (m, 8H), 0.95 (t, 12H).

Crystallographic Data. Complexes 1−3 were glued to a thin glass fiber with epoxy resin and collected on a Bruker APEX II diffractometer equipped with a fine−focus, 2.0−kW sealed−tube X−ray source (Mo Kα radiation, λ = 0.7103 Å) operating at 50 kV and 30 mA at 273 K. The crystallographic collection and refinement parameters for complexes 1 and 3 are listed in Table 1.

The structure of complex 2 was omitted because it resembles the one reported. The empirical absorption correction was based on equivalent reflections, and other possible effects such as absorption by the glass fiber were simultaneously corrected. Each structure was solved by direct methods followed by successive difference Fourier methods. All non-hydrogen atoms were refined anisotropically. Computations were performed using SMART, and final full-matrix refinements were against $F^2$. The SMART software was used for collecting frames of data, indexing reflections, and determining lattice constants, SADABS for integration of the intensities of the reflections and scaling, SADABS for absorption correction, and SHELXTL for space groups and structure determinations, refinements, graphics, and structure reporting.

**Electrochemistry.** Cyclic voltammetry (CV) was carried out with a CH Instruments 730A electrochemical analyzer. A three-electrode system consisting of a platinum working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode was used. The reference electrode was separated from the bulk solution by a fritted-glass bridge filled with the solvent/supporting electrolyte mixture. The CV data were recorded with a scan rate ranging from 100 mV s$^{-1}$ to 1 V s$^{-1}$. All potential values were reported versus the ferrocene/ferrocenium ion ($\text{Fc}^+/\text{Fc}$) or under heating conditions. The electronic absorption spectra of complexes 1–3 showed a characteristic IR absorption of the nitrosyl group ($\nu_{\text{NO}}$) at 1799 cm$^{-1}$ for [Fe$_4$S$_3$(NO)$_7$]$_2^-$ and at 1794 cm$^{-1}$ for [PPN]$_2$[Fe$_8$S$_6$-NO$_3$]$_3$. The FTIR spectrum of complex 2 showed a NO stretching frequency at 1799 cm$^{-1}$.

**Results and Discussion.**

**Synthesis of the Complexes.** It has been demonstrated that iron–sulfur nitrosyl clusters can be synthesized by the reactions of ferrous compounds, nitrosyl donor compounds, and sulfur donor reagents at room temperature or under heating conditions. In order to prepare and isolate new complexes of iron–sulfur (selenium) nitrosyl clusters and to investigate their properties, solvent-thermal reactions at high pressure were carried out under a nitrogen atmosphere and monitored by FTIR spectroscopy. Complex 1 was prepared by the reaction of 1 equiv of [(n-Bu)$_2$Se]$_2$N[Fe( CO)$_3$NO]$_5$ and 4 equiv of selenium in methanol. Upon reaction, the characteristic IR absorptions of the nitrosyl groups ($\nu_{\text{NO}}$) were shifted to lower frequencies as the carbonyls were substituted by selenium. Meanwhile, the orange reaction solution gradually turned to dark black. The observations are consistent with the results obtained from NMR and single-crystal X-ray diffraction. Complex 1 was obtained as a black solid with 85% yield. In order to prove the generality of this new synthetic method, a hexanuclear iron–sulfur nitrosyl cluster, 2, was synthesized using similar solvent-thermal reactions with sulfur donor reagents in high yield of 92%, and a tetranuclear cluster, 3, was also prepared by the solvent-thermal reaction of FeCl$_2$·4H$_2$O, thiourea, (CH$_3$)$_4$NCl, and NaNO$_2$ in methanol with 88% yield. Complexes 1–3 are all fairly stable in the solid state and in solution under air. Single crystals of complexes 1–3 suitable for X-ray diffraction analysis were obtained by the slow diffusion of diethyl ether into an acetonitrile solution at $-35^\circ C$. Complexes 1 and 2 are soluble in most polar organic solvents including acetonitrile, dichloromethane, and tetrahydrofuran but are insoluble in methanol, ethyl ether, and hexane, while complex 3 is more or less soluble in all organic solvents. The electronic absorption spectra of complexes 1–3 suitable for X-ray diffraction analysis were obtained by the slow diffusion of diethyl ether into an acetonitrile solution at $-35^\circ C$. Complexes 1 and 2 are soluble in most polar organic solvents including acetonitrile, dichloromethane, and tetrahydrofuran but are insoluble in methanol, ethyl ether, and hexane, while complex 3 is more or less soluble in all organic solvents. The electronic absorption spectra of complexes 1–3 were measured in acetonitrile. As shown in Figure 1, complex 1 shows a medium band at 288 nm and a weak band at 554 nm. The absorptions mainly arise from the transitions between orbitals delocalized over the Fe-Se cluster, the ligand-to-metal charge transfer (LMCT), $\pi^*_{\text{NO}}$-$d_{\text{Fe}}$, and the metal-to-ligand charge transfer (MLCT), $d_{\text{Fe}}$-$\pi_{\text{NO}}$. The bands over 400 nm are ascribed to the LMCT, while the bands at higher energy are

**Table 1. Crystallographic Collection and Refinement Parameters for 1 and 3**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Formula</th>
<th>Value</th>
</tr>
</thead>
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<tr>
<td>M$_n$</td>
<td>C$<em>{32}$H$</em>{72}$N$_8$O$_6$Se$_6$Fe$_6$</td>
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<tr>
<td>Z</td>
<td>C$<em>{4}$H$</em>{12}$N$_8$O$_7$S$_3$Fe$_4$</td>
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<td>Space group</td>
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</tr>
<tr>
<td>a [Å]</td>
<td>12.0207(6)</td>
<td>1.025</td>
</tr>
<tr>
<td>b [Å]</td>
<td>11.8711(6)</td>
<td>0.0527</td>
</tr>
<tr>
<td>c [Å]</td>
<td>18.5002(12)</td>
<td>0.0419</td>
</tr>
<tr>
<td>$\alpha$ [deg]</td>
<td>95.416(4)</td>
<td>0.0779</td>
</tr>
<tr>
<td>$\beta$ [deg]</td>
<td>95.416(4)</td>
<td>0.0779</td>
</tr>
<tr>
<td>$\gamma$ [deg]</td>
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<td>0.0779</td>
</tr>
<tr>
<td>V [Å$^3$]</td>
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</tr>
<tr>
<td>d(I &gt; 2$\sigma$(I))</td>
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<td>1.025</td>
</tr>
<tr>
<td>wR2</td>
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<td>2.089</td>
</tr>
<tr>
<td>$\theta$ [mm$^{-1}$]</td>
<td>5.811</td>
<td>3.333</td>
</tr>
<tr>
<td>R (I &gt; 2$\sigma$(I))</td>
<td>0.995</td>
<td>1.025</td>
</tr>
</tbody>
</table>

thought to be from MLCT and the transitions within the Fe–Se cluster. Similarly, complex 2 shows two medium bands at 259 and 297 nm and a weak band at 552 nm, whereas complex 3 displays four bands at 265, 357, 425, and 562 nm.

**Structural Studies.** The molecular structures of complexes 1–3 were determined by X-ray diffraction analysis, and it was found that the structural parameters of complex 2 resembled the one reported. The selected bond lengths and bond angles are listed in Table 2. The crystal structure of 1 is monoclinic and crystallized in a P2₁/n space group with two molecules per unit cell. As shown in Figure 2, two parallel “chair-shaped” structures, consisting of three iron and three selenium atoms, are connected by Fe–Se bonds with an average distance of 2.341 Å, and each iron center is bonded to three selenium atoms and a nitrogen atom from the nitrosyl ligand with a pseudo-tetrahedral center geometry. The [Fe₆Se₆(NO)₆]²⁻ cluster had been prepared previously with different counterions in a more complicated procedure. For the crystal structure of 3, no differences could be attributed to effects of the counterion besides the packing effects, which is related with the distortions of the Fe₆S₆ core.

The average Fe–Fe distance of 2.730 Å for 1 suggests that there is fairly strong interaction between the two iron centers. It is longer than the relevant value of 2.644 Å for 2 because the radius of the selenium atom is larger than that of sulfur. This is in agreement with the average value of 2.341 Å for the Fe–Se interactions in the [Fe₆Se₆(NO)₆]²⁻ cluster and 2.220 Å for the Fe–S interactions in the [Fe₆S₆(NO)₆]²⁻ cluster. Interestingly, the average Fe–Fe distance of 2.644 Å for [Fe₆S₆(NO)₆]²⁻, even 2.730 Å for [Fe₆Se₆(NO)₆]²⁻ or 2.705 Å for 3, is clearly shorter than the relevant value of 2.764 Å for diamin [Fe₆S₆(NO)₆]²⁻. This difference can be explained by the following. On the one hand, the [Fe₆Se₆(NO)₆]²⁻ and [Fe₆S₆(NO)₆]²⁻ clusters possess structural cores different from that of [Fe₆S₆(NO)₆]²⁻; on the other hand, the highest occupied molecular orbital of [Fe₆S₆(NO)₆]²⁻ contains an unpaired electron, which has an antibonding character involving all pairs of iron atoms of the Fe₆S₆ core, leading to an increase of the Fe–Fe bond lengths, while the [Fe₆S₆(NO)₆]²⁻ and [Fe₆S₆(NO)₆]²⁻ clusters are similar to 3, which are EPR-silent and have no unpaired electrons, as demonstrated by their perfect ¹H NMR spectra. This similar phenomenon has also been observed by Dahl and co-workers in the clusters [Fe₆S₆(NO)₆] and [Fe₆S₆(NO)₆].

The Fe–N bond distances for compound 1 range from 1.661 to 1.665 Å with an average of 1.663 Å. It is similar to the value of 1.667 Å in compound 2, in which the Fe–N bond distances range from 1.659 to 1.672 Å. Accordingly, the N–O bond lengths in compound 1 range from 1.72 to 1.86 Å, with an average of 1.83 Å, which is also similar to the mean of 1.82 Å (from 1.678 to 1.973 Å) in compound 2. When [Fe₆S₆(NO)₆]²⁻ and [Fe₆S₆(NO)₆]²⁻ (3) are compared, the Fe–N interactions are evidently strengthened in the dianion (average value: 1.646 vs 1.671 Å in the mono-anion) owing to more back-donation from dFe to π*NO. On the other hand, the average N–O bond lengths are 1.176 Å for [Fe₆S₆(NO)₆]²⁻ and 1.166 Å for 3, an opposite trend. These observations are consistent with the results of the IR spectra, which show that the absorptions of nitrosyl groups (νNO) appear at higher frequencies for complex 3.

The Fe–N–O bond angles range from 174.5° to 178.9° with an average of 176.5°, which is close to linear. This indicates that the nitrosyl moieties exhibit sp-hybridized NO⁺ character, which means that a considerable amount of charge transfer between NO and the metal took place. The average Fe–N–O bond angle of 176.5° in complex 1 is similar to the average values of 174.4° in complex 2, 176.9° in [Fe₆S₆(NO)₆]²⁻, 177.6° in [Fe₆S₆(NO)₆]²⁻, and 177.5° in [Fe₆S₆(NO)₆]²⁻ and the Fe–N–O bond angles of 177.6° and 178.3° arising from the apical Fe(NO) in [Fe₆S₆(NO)₆]²⁻ and complex 3. However, it is clearly longer than the average Fe–N–O bond angles of 167.9° and 166.6° arising from the three sets of Fe(NO)₂ of [Fe₆S₆(NO)₆]²⁻ and complex 3, respectively. When comparing complex 3 with other Roussin’s black salts, no differences could be attributed to the effects of the counterion besides the packing effects. These results show that the Fe–N–O bond angles of iron–sulfur (selenium) clusters are irrelevant to their dimension and charge but relevant to the number of nitrosyls attached to the iron atoms and the localized symmetry of the iron atoms.

**Electrochemical Properties.** The electrochemistry of complexes 1–3 was studied by CV, and the data are listed in Table 3. As shown in Figure 3, complex 1 shows two cathodic current peaks at Epc = −0.42 and −1.36 V and three anodic peaks at Epa = −0.04, −0.38, and −1.30 V; the peak at Epc = −0.42 V is unusually strong with a full scan range from 0.40 to −1.80 V. In order to interpret the abnormal phenomenon, the CVs were scanned with different potential ranges. Interestingly, two quasi-reversible

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reductions with half-wave potentials of $-0.41$ and $-1.33$ V with $E_{pc}/E_{pa}$ separations of 60 and 70 mV were found when the range was set between $-0.20$ and $-1.80$ V. In addition, the cyclic voltammogram of the first reduction ($E_{pc} = -0.42$ V) and the two corresponding oxidation peaks ($E_{pa} = -0.04$ and $-0.38$ V) showed no change when the scan potential was set from $+0.4$ to $-0.7$ V, but the oxidation peak at $-0.04$ V was not observed when the potential was switched off at $-1.0$ V, showing that the oxidation peak at $-0.04$ V is the product of the reduction at $-0.42$ V. These results indicate that the intensity of the unusually strong peak at $E_{pc} = -0.42$ V is a result of at least three processes. One is the quasi-reversible reduction at $E_{1/2} = -0.41$ V, and the other two are from an irreversible electrochemical process that occurred at $E_{pc} = -0.42$ V, in which the compound went through a typical electron transfer and chemical reaction (ECT) mechanism, of which its product is easier to reduce than the original one, resulting in an overlap of the reduction potentials and, subsequently, a very strong peak. The peak at $E_{pa} = -0.04$ V is the product from such a chemical reaction.

The redox behavior of compound 2 shown in Figure 4 exhibits two cathodic current peaks at $E_{pc} = -0.30$ and $-1.29$ V and three anodic peaks at $E_{pa} = 0.08$, $-0.23$, and $-1.19$ V when scanned from 0.40 to $-1.80$ V with a scan
rate of 100 mV s\(^{-1}\). It is similar to compound 1 in that the first reduction peak is much stronger than the second one. The cyclic voltammograms were also recorded using various scan rates from 0.1 to 1.0 V s\(^{-1}\). As shown in Figure 4, when faster scan rates were applied, the first reduction peak was separated to two reductions. Meanwhile, the faster the scan rate, the clearer the separation observed between the two reduction peaks. However, the peaks that arose from the ECE process did not disappear even at a scan rate of 1 V s\(^{-1}\), which indicates that the chemical step is quite fast. These observations are different from the reported cyclic voltammograms with the half-wave potentials of \(-0.87\) and \(-1.70\) V for (PPN)\(_2\)[Fe\(_6\)S\(_6\)−(NO)\(_6\)]\(_3\) and \(-0.11, -0.91, -1.08, -1.58, \) and \(-1.82\) V for (Et\(_4\)N)\(_2\)[Fe\(_6\)S\(_6\)NO]\(_2\). For the former, a possible reason is that a wider scan range (+0.40 to \(-1.80\) V) was used in our experiments than the one reported (0.0 to \(-1.80\) V) in which one of redox courses could not be observed. For the latter, a reasonable explanation is that some factors, such as the counterion, electrolyte, electrode, and different starting scan potentials, caused two sets of one-electron reductions to overlap under our experimental conditions. Compound 3 bears three quasi-reversible reductions with half-wave potentials of \(-1.09, -1.71, \) and \(-2.21\) V, which is similar to the values \(-0.86, -1.44, \) and \(-1.93\) V reported for (Et\(_4\)N)[Fe\(_4\)S\(_3\)NO].\(^{5c}\)

Conclusions

In summary, iron–selenium and iron–sulfur nitrosyl clusters [(n-Bu)\(_4\)N][Fe\(_6\)Se\(_6\)(NO)]\(_3\) (1), [(n-Bu)\(_4\)N][Fe\(_6\)Se\(_6\)−(NO)]\(_3\) (2), and (Me\(_4\)N)[Fe\(_6\)S\(_6\)(NO)]\(_3\) (3) have been synthesized by efficient solvent-thermal reactions, and their structures and properties have been studied by IR, UV−vis, \(^{1}\)H NMR, electrochemistry, and single-crystal X-ray diffraction analysis. IR spectra of complexes 1 and 2 all display one strong characteristic NO stretching frequency (\(\nu_{\text{NO}}\)) in solution with the characteristic of NO\(^+\), while the IR spectrum of complex 3 displays three absorptions. The electronic absorption spectra show different bands in the range of 259–562 nm, which are assigned to the transitions between orbitals delocalized over the Fe–S cluster, the LMCT, \(\pi^*_{\text{NO}}–d_{\text{Fe}}\), and the MLCT, \(d_{\text{Fe}}–\pi^*_{\text{NO}}\). Single-crystal X-ray structural analysis reveals that complex 1 crystallizes in the monoclinic \(P2(1)/n\) space group with two molecules per unit cell. Each iron center is bonded to three selenium atoms and a nitrogen atom from the nitrosyl ligand with a pseudotetrahedral center geometry. The two parallel “chair-shaped” structures, consisting of three iron and three selenium atoms, are connected by Fe–Se bonds. CV of compounds 1 and 2 display two cathodic and three anodic current peaks with an unusually strong cathodic peak. The experimental results indicate that the intensity of the unusually strong peak is a result of at least three processes. One is the quasi-reversible reduction, and the other two are from an irreversible electrochemical process, in which the compound went through a typical ECE mechanism. Compound 3 shows three quasi-reversible reductions.

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Supporting Information Available: IR and \(^{1}\)H NMR spectra of complexes 1–3 as well as the cyclic voltammogram and structural diagram of complex 3 and X-ray crystallographic files in CIF format for complexes 1 and 3. This material is available free of charge via the Internet at http://pubs.acs.org.