Synthesis and Characterization of a Tetranickel Complex Supported by a Dithiolate Framework with Pendant Ether Moieties

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ABSTRACT. We report here the synthesis of a novel dithiolate ligand framework with pendant ether groups. Metallation reactions were performed with nickel(II) precursors, in the presence of base, leading to a tetranuclear nickel(II) species, as evidenced by single crystal X-ray diffraction studies. A C_{2v} symmetric structure is observed, with the Ni^{II} centers in a square arrangement. Each Ni^{II} center is coordinated by four bridging thiolates.

1. Introduction

Nature uses metalloproteins to perform a variety of difficult reactions, such as the activation of small molecules (CO_2 , N_2 , H_2O), near the thermodynamic potential and with high turnover frequencies.¹⁻¹¹ These reactions play important roles in the global biological carbon, nitrogen,

and oxygen cycles, and they involve multiple electron and proton transfer steps. The protein matrix is capable of controlling the coordination environment around the metal sites generating multi-metallic motifs, with pendant oxygen or nitrogen groups, which bind the substrate simultaneously and provide multiple equivalents of electrons to facilitate these transformations. For example, CO₂ binding and catalysis in Ni,Fe-CO-dehydrogenase involves bifunctional activation of the substrate by the two metal centers and additional stabilization from proton relays present in the second coordination sphere.² In a similar fashion, the pendant amine present in [FeFe]-hydrogenase was shown to assist in proton transfer steps and facilitate the hydrogen evolution reaction.^{5,10} These architectural features are instrumental in controlling the protein activity, and they have inspired the development of related biomimetic systems.¹²⁻¹⁷

A variety of multimetallic biomimetic systems have been reported. Metallothiolates have been commonly used as versatile S-donor metalloligands in coordination, bioinorganic, and organometallic chemistry due to the propensity of the thiolates ligands to bind multiple metal centers.¹⁸ These metallothiolates units lead to an assortment of multinuclear transition metal complexes. Figure 1 illustrates the previously reported nickel complexes supported by norbornanedithiolate-based ligand frameworks. The norbornanedithiolate-Ni motif has been popularized by Millar and coworkers, who reported the synthesis and chemical properties of a stable monomeric Ni(II)-tetrathiolate complex which is readily oxidized to a stable Ni(III)-tetrathiolate species at biologically relevant redox potentials ($E_{1/2} = -0.46$ V vs SCE).¹⁹ Henkel and coworkers have reported that the air oxidation of the mononuclear norbornanedithiolate-Ni complex leads to the formation of the tetranuclear nickel complex (Figure 1).²⁰ Tatsumi and coworkers have reported the concomitant formation of dithiolate-bridged Fe–Ni–Fe trinuclear and Ni₃Fe tetranuclear complexes in the same reaction mixture.²¹ Other tetranickel complexes

supported by monoanionic thiolate ligands have been reported as well by Gaete, Henkel and coworkers.²²⁻²⁵ Additionally, although multimetallic complexes have been extensively studied, versions that also display proton relays are rare.^{18,22,26-30} In this context, the development of thiolate ligand frameworks with pendant ether groups is of interest. We report here the synthesis and characterization of a tetranuclear nickel(II) complex supported by a 1,2-dithiolate framework with pendant ether moieties.

Figure 1. Previously reported nickel complexes supported by norbornanedithiolate-based ligand frameworks and tetranickel complexes supported by monoanionic thiolate ligands.

2. Materials and Methods

All manipulations of air and moisture sensitive materials were conducted under a nitrogen atmosphere in a Vacuum Atmospheres drybox or on a dual manifold Schlenk line. The glassware was oven-dried prior to use. All solvents were degassed with nitrogen and passed through activated alumina columns and stored over 4Å Linde-type molecular sieves. Deuterated solvents were dried over 4Å Linde-type molecular sieves prior to use. Proton NMR spectra were acquired at room temperature using Varian spectrometers and referenced to the residual ^1H resonances of the deuterated solvent (^1H : CDCl_3 , δ 7.26; C_6D_6 , δ 7.16; CD_2Cl_2 , δ 5.32; CD_3CN , δ 2.94) and are reported as parts per million relative to tetramethylsilane. Elemental analyses were performed by Robertson Microlit Laboratories Inc., Ledgewood, NJ. All the chemical reagents were purchased from commercial vendors and used without further purification. The compound 1,4-dihydro-1,4-epoxynaphthalene (**1**) was prepared according to the reported literature procedure.³¹

Synthesis of compound 3

A 100 mL oven dried 3-neck flask fitted with a reflux condenser and a stir bar was allowed to cool under vacuum. The flask was then refilled with nitrogen and charged with sulfur (154 mg, 4.8 mmol), **1** (229 mg, 1.59 mmol), and $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ (8 mg, 0.034 mmol). Dimethylformamide (7 mL) was added via syringe. The reaction mixture was refluxed at 120 °C for 6 hours. The cooled reaction mixture was eluted through alumina with chloroform (50 mL) and washed with water (10×100 mL). The organic layer was dried with anhydrous Na_2SO_4 . The volatiles were removed under vacuum to generate a mixture of **2** as an olive-green solid (257 mg, ~65% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.34–7.30 (m, 2H, aryl), 7.24–7.20 (m, 2H, aryl), 5.46 (s, 2H,

CHO), 4.21 (s, 2H, *CHS*). The mixture of **2** was used in the next step without further purification.

A 100 mL oven dried 3-neck flask fitted with a reflux condenser and a stir bar was allowed to cool under vacuum. The flask was then refilled with nitrogen, charged with a mixture of **2** (441 mg, ~2.0 mmol), and tetrahydrofuran (3 mL) to give a brown solution. Super-hydride™ (10 mL, 10 mmol) was added dropwise to the brown solution, which prompted a color change to yellow and vigorous bubbling. The reaction mixture was heated to 65 °C for 24 hours. The solution was allowed to cool and quenched with 1M hydrochloric acid (10 mL, 10 mmol) and extracted with diethyl ether (3 × 30 mL). The combined organic layers were washed with water (3 × 50 mL) and dried with Na₂SO₄. Upon removal of the volatiles, compound **3** was isolated as an off white oil (240 mg, 70%). ¹H NMR (500 MHz, CDCl₃) δ 7.34–7.30 (m, 2H, aryl), 7.24–7.20 (m, 2H, aryl), 5.22 (s, 2H, *CHO*), 3.30 (dd, 2H, *CHS*, *J* = 6.2, 2.0 Hz), 2.18 (dd, 2H, *SH*, *J* = 6.2, 2.0 Hz). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 143.5, 127.5, 119.6, 88.3, 45.9.

Synthesis of compound 4

In a nitrogen-filled glove box a 20 mL vial was charged with **3** (16.8 mg, 0.079 mmol), methanol (2 mL) and acetonitrile (4 mL). The solution was transferred to a 50 mL Schlenk flask equipped with a magnetic stir bar and connected to the Schlenk line. Under nitrogen, NiCl₂(H₂O)₆ (10.3 mg, 0.045 mmol) was added, prompting a color change to red. The reaction was allowed to stir at room temperature overnight. The volatiles were removed under vacuum and the evacuated flask was brought into the nitrogen-filled glove box. The material was washed with diethyl ether and tetrahydrofuran to remove any soluble impurities. The residue was dissolved in pyridine (5 mL)

and was allowed to stir at room temperature for one hour. The solvent was removed under vacuum. The resultant red solid was washed with diethyl ether, dissolved in toluene (5 mL), and filtered to remove insoluble impurities. The solution was diffused with pentane over the course of 24 hours to afford the product as fine red needles (5 mg, 20% yield). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.27–7.16 (m, 16H, aryl), 5.26 (s, 4H, CHO), 5.11 (s, 4H, CHO), 3.46 (br, 4H, CHS), 2.76 (br, 4H, CHS). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2) δ 144.6, 142.5, 127.9, 127.7, 120.3, 120.1, 88.0, 85.4, 61.1, 59.1. Anal. calcd for $\text{C}_{40}\text{H}_{32}\text{Ni}_4\text{O}_4\text{S}_8$: C, 44.99; H, 3.02. Found: C, 44.79; H, 3.06.

Crystal structure determination

The single-crystal X-ray diffraction data were collected on a Bruker SMART APEX DUO 3-circle platform diffractometer, equipped with an APEX II CCD detector, using Mo $\text{K}\alpha$ radiation (TRIUMPH curved-crystal monochromator) from a fine-focus tube. The diffractometer was equipped with an Oxford Cryosystems Cryostream 700 apparatus for low-temperature data collection. The frames were integrated using the SAINT algorithm to give the hkl files corrected for Lp/decay .³² The absorption correction was performed using the SADABS program.^{33,34} The structures were solved by intrinsic phasing and refined on F^2 using the Bruker SHELXTL Software Package and ShelXle.³⁵⁻³⁹ All non-hydrogen atoms were refined anisotropically.

3. Results and Discussion

The novel ligand **3** can be synthesized in three steps from commercially available starting materials (Scheme 1). The *in-situ* generated benzyne species undergoes a Diels-Alder reaction with excess furan to form 1,4-dihydro-1,4-epoxynaphthalene (**1**) using a reported literature procedure.^{31,40} This species reacts with elemental sulfur in the presence of $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ to form a mixture of exo-trithiolane and exo-pentathiolane (**2**), which was used in the next step without further purification. The reduction of the thiolane mixture (**2**) with superhydrideTM generates the corresponding dithiol **3** upon acidic workup. This methodology has been reported for the preparation of C-substituted analogues, bicyclo[2.2.1]-heptane-2,3-dithiol species.⁴¹ Several 1D and 2D ^1H and ^{13}C NMR experiments were performed, to confirm the assignment of the peaks (see SI; Figures S1–S5).

Scheme 1. Synthesis of a tetranickel(II) complex supported by a dithiolate ligand framework with pendant ether groups.

Figure 2. ORTEP drawing of **4** shown with 50% thermal ellipsoids; side (a), and top (b) views, and the coordination environment of the Ni₄S₈ square unit ((c) and (d)). Hydrogen atoms and solvent molecules were omitted for clarity.

With the novel ligand **3** in hand, metallation reactions were performed with nickel(II) starting materials. Under an inert atmosphere, [Ni(H₂O)₆]Cl₂ was added to a solution of ligand **3** in methanol/diethyl ether mixture, leading to an immediate color change from colorless to red. The generated red solid was dissolved in pyridine and then the volatiles were removed under vacuum. The crude mixture was extracted into toluene and filtered. Diffusion with pentane over 24 h afforded X-ray quality crystals. Single crystal X-ray diffraction studies revealed a

tetranuclear species **4** of C_{2v} symmetry, with the Ni^{II} centers displaying a square arrangement, and each Ni^{II} center coordinated by four bridging thiolates (Figure 2). Data collection parameters and selected bond lengths are listed in Tables 1 and 2, respectively. Although observed previously for Ni thiolates,²⁰⁻²⁴ this structural motif is rare. In the solid state, the Ni^{II} ions feature a pseudo square planar coordination environment ($\Sigma(L-Ni(1)-L) = 359.2(2)^\circ$; $\Sigma(L-Ni(2)-L) = 354.6(2)^\circ$; $\Sigma(L-Ni(3)-L) = 359.0(2)^\circ$; $\Sigma(L-Ni(4)-L) = 356.0(2)^\circ$). The Ni–S bond lengths corresponding to Ni(1), Ni(2), and Ni(3) are approximately 2.22 Å, which are typical of Ni^{II} –S single bonds.^{18,42,43} The Ni–S bond lengths corresponding to Ni(4) appear somewhat shorter, approximately 2.16 Å, which are similar to the Ni–S bond lengths observed previously in nickel(II) dithiolene complexes.⁴⁴⁻⁴⁶ We attribute this to the strained geometry of the tetranickel cluster. The C–S bond lengths are 1.83(2) Å, consistent with C–S single bonds.⁴⁷ The adjacent Ni–Ni distances are between 2.6 and 2.7 Å (Table 2), which are slightly longer than Ni–Ni single bonds (between 2.3 and 2.5 Å).⁴⁸⁻⁵³ The Ni(1)–Ni(3) and Ni(2)–Ni(4) distances are 3.504(2) and 3.993(1) Å, respectively. The Ni^{II} centers displaying an almost perfect square arrangement; the Ni(1)–Ni(2)–Ni(3)–Ni(4) torsion angle is 0.8(1)°.

Chemical formula	C ₉₀ H ₈₃ NNi ₈ O ₁₀ S ₁₆
Formula weight	2321.21 g/mol
Crystal system	monoclinic
Space group	<i>P</i> 1 2 ₁ /n 1
<i>a</i> (Å)	17.7449(6)
<i>b</i> (Å)	13.8337(5)
<i>c</i> (Å)	18.9902(6)
α (°)	90
β (°)	106.2440(11)
γ (°)	90
Volume (Å ³)	4475.6(3)
<i>Z</i>	2
<i>D</i> _{calc} (g cm ⁻³)	1.722
<i>m</i> (Mo K α) (mm ⁻¹)	2.078
<i>F</i> (000)	2380
Reflections collected	86247
Independent reflections	10665 (<i>R</i> _{int} = 0.1240)
<i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>))	0.0588
<i>wR</i> ₂ (all data)	0.1679
Goodness of fit (GOF) on <i>F</i> ²	1.022

Table 1. Crystallographic data for compound **4**.

Ni(1)	Ni(1)–S(1)	2.2350(17)	S(1)–Ni(1)–S(6)	99.26(6)
	Ni(1)–S(2)	2.1986(17)	S(6)–Ni(1)–S(8)	81.15(6)
	Ni(1)–S(6)	2.2196(16)	S(2)–Ni(1)–S(8)	97.90(6)
	Ni(1)–S(8)	2.2446(16)	S(1)–Ni(1)–S(2)	80.87(6)
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Ni(2)	Ni(2)–S(1)	2.1819(17)	S(1)–Ni(2)–S(2)	81.73(6)
	Ni(2)–S(2)	2.2132(16)	S(2)–Ni(2)–S(4)	96.85(6)
	Ni(2)–S(3)	2.2083(16)	S(4)–Ni(2)–S(3)	80.99(6)
	Ni(2)–S(4)	2.2125(17)	S(3)–Ni(2)–S(1)	95.00(6)
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Ni(3)	Ni(3)–S(3)	2.2012(16)	S(3)–Ni(3)–S(4)	81.31(6)
	Ni(3)–S(4)	2.2051(16)	S(4)–Ni(3)–S(7)	97.91(6)
	Ni(3)–S(5)	2.2340(16)	S(7)–Ni(3)–S(5)	79.94(6)
	Ni(3)–S(7)	2.2363(16)	S(5)–Ni(3)–S(3)	99.83(6)
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Ni(4)	Ni(4)–S(5)	2.1650(16)	S(5)–Ni(4)–S(6)	94.14(6)
	Ni(4)–S(6)	2.1597(16)	S(6)–Ni(4)–S(8)	84.45(6)
	Ni(4)–S(7)	2.1636(16)	S(8)–Ni(4)–S(7)	94.31(6)
	Ni(4)–S(8)	2.1612(16)	S(7)–Ni(4)–S(5)	83.12(6)
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	Ni(1)–Ni(2)	2.6237(11)	Ni(1)–Ni(2)–Ni(3)	82.06(3)
	Ni(2)–Ni(3)	2.7134(10)	Ni(2)–Ni(3)–Ni(4)	96.97(3)
	Ni(3)–Ni(4)	2.6188(10)	Ni(3)–Ni(4)–Ni(1)	83.01(3)
	Ni(4)–Ni(1)	2.6689(10)	Ni(4)–Ni(1)–Ni(2)	97.96(3)

Table 2. Selected bond lengths (Å) and angles (°) for complex **4**.

^1H NMR spectroscopic characterization of **4** in CD_2Cl_2 shows four peaks in the aromatic region between δ 7.27 and 7.16 ppm, as expected for the four inequivalent aryl protons (two for each symmetry equivalent ligand moieties) (Figure 3). Two additional singlets are observed at δ 5.26 and 5.11 ppm in a 1:1 ratio, corresponding to the inequivalent *CHO* moieties (four protons each). The ^1H NMR of **4** in CD_2Cl_2 also displays two additional peaks at δ 3.46 and 2.76 ppm in a 1:1 ratio, corresponding to the inequivalent *CHS* moieties (four protons each). The NMR spectroscopy data is consistent with a C_{2v} geometry of compound **4** in solution, suggesting that the tetranuclear moiety remains intact and preserves its solid state geometry.

Figure 3. 500 MHz ^1H NMR spectrum of **4** in CD_2Cl_2 .

X-ray diffraction studies of this complex show that the nickel centers are site differentiated. Ni(4) has two ether moieties in close proximity to the metal complex (distances of 4.1(1) Å), whereas Ni(1) and Ni(3) have only one ether moiety at distances of 3.0(1) Å, and Ni(2) has none. The nickel complexes with pendant amines display non-bonding Ni–N distances of 3.1–3.4 Å,^{47,54} which are in the same range as the Ni–O distances observed in complex **4**. The low yield of complex **4**, as well as its instability in most common solvents, precluded further reactivity studies.

4. Conclusions

In summary, a novel dithiolate ligand framework with pendant ether groups has been synthesized, and its coordination chemistry was explored. Single crystal X-ray diffraction studies revealed a tetranuclear species with the nickel centers displaying a square arrangement, and each Ni^{II} center coordinated by four bridging thiolates. This synthetic strategy is expected to be useful for the preparation of dithiolates with other pendant basic groups to mimic the active sites of metalloproteins.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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