SYNTHESIS AND CHARACTERIZATION OF GROUP VI METAL COMPLEXES
FOR NON-CLASSICAL OXYGENATION REACTIONS

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by

Leila Amery Galang Ranis

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Seth N. Brown, Director

Graduate Program in Chemistry and Biochemistry
Notre Dame, Indiana
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Abstract

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Metal complexes supported by redox-active ligands have the ability to promote multielectron transfer reactions. Advances in multielectron transfer reactions have significant impacts in catalysis and renewable energy storage. The synthesis and characterization of group VI metal complexes using the DOPO ligand, 2,4,6,8-tetra-tert-butyl-1-oxo-1H-phenoxazin-9-olate, is described, and their reactivity in non-classical oxygenation reactions is examined.

H(DOPO\(^0\)) is prepared using a modified literature procedure, where 2,6-dihydroxy-3,5-di-tert-butylaniline and 3,5-di-tert-butylcatechol are reacted at room temperature in the presence of 10 mol\% triethylamine under aerobic conditions. Cr(DOPO)\(_2\) is synthesized by the reaction of H(DOPO\(^0\)) with chromocene. Its crystal structure reveals \(C_{2v}\) symmetry, with one partially reduced ligand, DOPO\(^{SQ}\), more tightly bonded to Cr than the other fully oxidized ligand, DOPO\(^Q\). The magnetic susceptibility of Cr(DOPO)\(_2\) is measured both as a solid and as a toluene solution, showing Curie-Weiss paramagnetism with some temperature independent paramagnetism in the solid.
\[
\text{Pb(DOPO}^\text{Q})_2 \text{ is prepared by dissolving lead acetate trihydrate in a heated methanol solution with H(DOPO}^\text{Q}). \text{ Its geometry differs from most homoleptic DOPO metal complexes, with the DOPO ligands forming a } \kappa^2\text{-like coordination to Pb due to the stereochemically active lone pair of electrons in the 6s metal orbital. Pb(DOPO}^\text{Q})_2 \text{ is employed in the synthesis of M(DOPO)_2 (M = Mo, W) from M}_2\text{Br}_4(\text{CO})_8. \text{ The crystal structures of Mo(DOPO)_2 and W(DOPO)_2 are isomorphous, with the DOPO ligands coordinated in a meridional fashion to the corresponding metal centers. } ^1\text{H and } ^{13}\text{C NMR spectroscopy along with metrical data from x-ray diffraction studies support a fully reduced catecholate form for both ligands.}
\]

\[
\text{Reaction of the molybdenum and tungsten complexes, M(DOPO}^{\text{Cat}}_\text{2}, \text{ with excess Me}_3\text{NO gives MO}_2(\text{DOPO})_2, \text{ with both DOPO ligands in the fully oxidized quinonoid form, in addition to paramagnetic products. Reaction of M(DOPO}^{\text{Cat}}_\text{2} \text{ with a weaker amine } N\text{-oxide such as NMO only gives traces of MO}_2(\text{DOPO})_2, \text{ with the major product being H(DOPO}^\text{Q}) \text{ and paramagnetic products. The molybdenum dioxo complex, MoO}_2(\text{DOPO}^\text{Q})_2, \text{ has been prepared independently from MoO}_2\text{Cl}_2(\text{dmf})_2 \text{ and Pb(DOPO}^\text{Q})_2. \text{ Addition of 2 equivalents of PPh}_3 \text{ to MoO}_2(\text{DOPO}^\text{Q})_2 \text{ results in regeneration of Mo(DOPO}^{\text{Cat}}_\text{2} \text{ and formation of OPPPh}_3 \text{ via the intermediacy of a PPh}_3\text{-containing species observable by NMR. Less bulk and more basic PMe}_2\text{Ph achieves the same net deoxygenation more rapidly, but without formation of detectable amounts of an intermediate.}
\]

\[
\text{Enterobactin is prepared using a modified procedure, and its reactivity with molybdenum(VI) is examined. A one-pot reaction of 2,3-bis(benzyloxy)benzoyl chloride with tris(N-trityl-L-serine) trilactone affords hexabenzylenterobactin directly. This}
\]
procedure consolidates the removal of the N-trityl protecting groups and amide bond formation between the trilactone backbone and the side chains into one facile step. While MoO$_2$(acac)$_2$ reacts with enterobactin, factors such as the limited solubility of enterobactin and aggregation of enterobactin-Mo complexes into oligomers inhibit the formation of a stable $C_3$-symmetric enterobactin-Mo(VI) complex.
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CHAPTER 1
INTRODUCTION

1.1 Activating Molecular Oxygen

Molecular oxygen is a thermodynamically powerful oxidant that may be employed in the conversion of alcohols into aldehydes or ketones and the functionalization of olefins and alkynes. Compared to common halogen-, hexavalent chromium-, and (per)manganate-based oxidizing agents, its byproducts (such as water) are relatively benign. Hence, it offers an environmentally friendly alternative for chemical synthesis. Conversely, evolution of O\(_2\) is a key step in renewable energy storage. For example, in photocatalytic water splitting\(^1\), solar energy is used to oxidize water into O\(_2\), while leftover protons (H\(^+\)) and electrons are funneled to a hydrogenase-like catalyst, which turns it into a form of chemical fuel (H\(_2\)).\(^1\)

Molecular oxygen is kinetically inert and therefore is a prime target for catalysis. The challenge lies in lowering the energetic barrier formed by the peroxo intermediate. Activating O\(_2\) requires four electrons, but redox processes usually only take place by single or two-electron transfers. In two-electron water oxidation, a peroxo intermediate is formed, and the subsequent oxidation to O\(_2\) has an overpotential of 0.543 V\(^2\) (Figure 1). The process requires 1.45 times more energy than the direct formation of O\(_2\) from H\(_2\)O. Hence, two-electron water oxidation and O\(_2\) reduction are thermodynamically less
favorable than the corresponding four-electron processes. The peroxo intermediate needs to be stabilized to allow for seamless conversion in either direction.

\[
\begin{array}{c}
+1.229 \text{ V} \\
-0.130 \text{ V} & +1.495 \text{ V} & +1.776 \text{ V} \\
\text{O}_2 & \rightarrow & \text{HO}_2 & \rightarrow & \text{H}_2\text{O}_2 & \rightarrow & \text{H}_2\text{O} \\
& & +0.682 \text{ V} \\
\end{array}
\]

**Figure 1.** Potentials for the two- and four-electron reduction of O\(_2\)

1.2 Non-Classical Oxygenation Reactions

A mononuclear metal complex is an attractive catalyst design; it would allow for facile synthesis and simpler mechanisms, but few metals are able to provide the four electrons needed to fully reduce O\(_2\).\(^3\) This can be addressed by taking a ‘non-classical’\(^4\) approach to redox processes. In a ‘classical’ oxygenation reaction, redox processes are localized at the site of bond making/breaking. In a ‘non-classical’ oxygenation reaction (Figure 2),\(^5\) the reducing ability comes from the ligand(s), and the metal center facilitates the flow of electrons from the redox-active ligand(s) to the substrate as well as forming new bonds to the substrate.

**Figure 2.** An example of a non-classical oxygenation reaction.\(^5\)

High coordination numbers may help stabilize the peroxo intermediate. The smaller bite angles of seven- or eight-coordinate metal complexes better accommodate
the short O-O bond length of the peroxo ligand. The loss of strain may lower the energy of the peroxo intermediate, making O$_2$ activation and water oxidation more efficient.

To be useful in chemical synthesis (Figure 3), the metal complex must be able to transfer oxygen to a substrate. Hence, it cannot lose its oxidizing power. However, fully oxidized ligands bind more weakly to the metal center than their reduced counterparts. For example, single electron oxidation of catechol bound- and amidophenolate bound-Sb(V) formed stable semiquinonoid species, [Ph$_3$Sb(L$^{SQ}$)]$^+$, but two electron oxidation resulted in the immediate dissociation of benzoquinone or iminoquinone from the metal center.$^6$ Free 3,5-di-tert-butyl-1,2-benzoquinone was also produced in the reaction of tris(di-tert-butyldietholate)molybdenum(VI), Mo(DBCat)$_3$, with O$_2$. $^7$ Polydentate ligands, such as pincer ligands, are ideal. They chelate to the metal center at multiple points, contributing to their stability. The ligands can also dangle and reattach, allowing for some flexibility, for instance, to relieve oxygen-oxygen repulsions or to decrease steric bulk for substrate attack.

**Figure 3.** Proposed scheme for the oxygenation of olefins catalyzed by Group VI metal complexes
1.3 Group VI Metal Complexes

This thesis describes the synthesis and characterization of group VI metal complexes using two redox-active ligands: 2,4,6,8-tetra-tert-butyl-1-oxo-1H-phenoxazin-9-olate, DOPO, and enterobactin (Figure 4). It also examines their reactivity in non-classical oxygenation reactions.

![Figure 4. Non-innocent ligands: H(DOPO\(^5\)) (Left) and Enterobactin (Right)](image)

Group VI metals were utilized because group VI metal dioxo complexes have exhibited reactivity in oxygenation reactions such as epoxidation of olefins and oxidation of sulfides.\(^{10}\) The reactivity of Mo(VI) and W(VI) metal complexes in non-classical oxygenation reactions is also currently being investigated.\(^4, 7b, 11\) These metals have d\(^0\) configurations; they do not have accessible electrons to participate in redox processes. Hence, oxidations of these metals must be ‘non-classical’ in nature, as there are no electrons to be removed.

The group VI metal complexes were synthesized with the following key design concepts: (1) The redox-active ligand(s) must collectively have at least four reducing equivalents. (2) High coordination numbers better stabilize the peroxo intermediate. (3)
Polychelating ligand(s) ensure that the catalyst retains its oxidizing ability by preventing dissociation of the ligands(s) in its (their) oxidized form(s).
CHAPTER 2

GROUP VI METAL COMPLEXES WITH 2,4,6,8-TETRA-TERT-BUTYL-1-OXO-1H-PHENOXAZIN-9-Olate, DOPO, AND THEIR REACTIVITY

2.1 DOPO

The redox properties of the \(N\)-(3,5-di-tert-butyl-2-oxyphenyl)-3,5-di-tert-butylquinoneimine (ONO) ligand have long been established,\(^\text{12}\) and several ONO metal complexes have been synthesized to mediate multielectron transfer reactions.\(^\text{13}\) The Heyduk group has synthesized W(ONO\text{Cat})\text{2} (Equation 1),\(^\text{14}\) and the Brown group has also prepared the Mo (and W) analogues from M(II) precursors and the lead salt of the oxidized ligand (Equation 2).\(^\text{15}\)

\[
\begin{align*}
\text{WCl}_6 + 2\text{H}_3\text{(ONO}\text{Cat}) \xrightarrow{\text{Toluene, reflux 16 h}} \text{W(ONO}\text{Cat})\text{2} + 6\text{HCl} \quad (\text{Eq. 1}) \quad 74\%
\end{align*}
\]

\[
\begin{align*}
\text{Pb(ONO}^O\text{)}\text{2} + 1/2\text{M}_2\text{Br}_4\text{(CO)}_8 \xrightarrow{\text{CHCl}_3, \text{r.t. 1 h}} \text{M(ONO}\text{Cat})\text{2} + \text{PbBr}_2 + 4\text{CO} \quad (\text{Eq. 2})
\end{align*}
\]

\[
\begin{align*}
\text{M} = \text{W} & \quad 41\% \\
\text{Mo} & \quad 54\%
\end{align*}
\]

However, upon reaction with various oxidants, the oxidized ligand readily detaches\(^\text{16}\) as H(ONO\text{O})\(^\text{17}\) and decomposes into phenoxazinone\(^\text{18}\) (Figure 5). It cyclizes to form an oxygen bridge between the two aromatic rings, thus, preventing its reattachment to the metal center. The loss of oxidizing power bars the metal complex from conducting
oxygen atom transfer reactions. The DOPO ligand circumvents this problem as the oxygen bridge is already in place.

![Figure 5](image)

**Figure 5.** Decomposition pathway of the ONO ligand

Several first row transition metal M(DOPO)$_2$ complexes have been synthesized but they all favored high spin structures with the ligands in their fully oxidized form, DOPO$^Q$. The aim is to examine whether the DOPO ligand can undergo two single electron redox processes, spanning three oxidation states (Figure 6), from a fully reduced trianionic state [DOPO$^\text{Cat}$]$^3^-$ to a partially oxidized dianionic intermediate [DOPO$^\text{SQ}$]$^2^-$ to a fully oxidized monoanionic form [DOPO$^Q$]. If so, each DOPO$^\text{Cat}$ ligand stores two reducing equivalents, and a bis-DOP$^\text{Cat}$ metal complex will have the four electrons needed to activate molecular oxygen.

![Figure 6](image)

**Figure 6.** Possible oxidation states of the DOPO ligand

We expect the tridentate ligands to adopt an octahedral geometry with group VI metals, which may allow for the formation of a higher coordinate peroxo ligated metal complex (Figure 7). Even in its fully oxidized form, the DOPO ligand is an anion. Hence, it binds strongly to the metal center, inhibiting ligand dissociation.
2.2 Experimental

Unless otherwise noted, all procedures were carried on the benchtop. When dry solvents were needed, chlorinated solvents and acetonitrile were dried over 4 Å molecular sieves, followed by CaH₂. Benzene and toluene were dried over sodium. Deuterated solvents were obtained from Cambridge Isotope Laboratories and dried using the same procedures as their protio analogues. All dry solvents were stored in the drybox prior to use. 2,6-Dihydroxy-3,5-di-tert-butylaniline was prepared using the method of Minkin and coworkers. W₂Br₄(CO)₈, Mo₂Br₄(CO)₈, and MoO₂Cl₂(dmf)₂ were prepared according to literature procedures. All other reagents were commercially available and used without further purification. Routine NMR spectra were measured on CDCl₃ solutions on a Varian VXR-300 or Bruker DPX-400 spectrometer. Chemical shifts for ¹H and ¹³C{¹H} spectra are reported in ppm downfield of TMS, with spectra referenced using the chemical shifts of the solvent residuals. Variable temperature NMR spectra were measured for a deuterated dichloromethane solution of Pb(DOPO⁰)₂ on a
Varian VXR-500. Infrared spectra were recorded as solids on a JASCO FT/IR-6300 spectrometer using an ATR cell. Optical spectra were measured as dichloromethane solutions using a 1 cm quartz cell on a Beckman DU-7500 or Jasco UV-670 spectrophotometer. ESI mass spectra were obtained using a Bruker micrTOF-Q II or Bruker micrTOF-II mass spectrometer, and peaks reported are the mass number of the most intense peak of isotope envelopes. Samples were injected as chloroform solutions. Elemental analyses were performed by Robertson Microlit Laboratories (Ledgewood, NJ).

**2,4,6,8-tetra-tert-butyl-9-hydroxy-1H-phenoxazin-1-one, H(DOPO<sup>Q</sup>).** In a 250 mL Erlenmeyer flask, 761.7 mg 3,5-di-tert-butylcatechol (Aldrich, 3.43 mmol) and 813.1 mg 2,6-di-hydroxy-3,5-di-tert-butylaniline (1 equiv) were dissolved in 25 mL benzene. A catalytic amount of triethylamine (Aldrich, 107 µL, 10 mol%) was added and the flask sealed with Parafilm. After stirring for 24 h, the solvent was evaporated off *in vacuo* at room temperature to give a purple oil that hardened into a glass. The residue was triturated with 5 mL methanol and suction filtered over a fine porosity glass frit. The solid was washed with 20 mL methanol and suction filtered to dryness. 380.8 mg of purple crystalline H(DOPO<sup>Q</sup>) is recovered (25%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, cf. lit.): δ 1.38, 1.48 (s, 18H each, tBu), 7.49 (s, 2H, ArH).

**Bis(2,4,6,8-tetra-tert-butyl-1,9-dioxophenoxazinato)lead(II), Pb(DOPO<sup>Q</sup>)<sub>2</sub>.** In a 250 mL round bottom flask, 122.1 mg lead acetate trihydrate (Aldrich, 0.322 mmol) and 280.2 mg H(DOPO<sup>Q</sup>) (1.99 equiv) were dissolved in 120 mL methanol. The flask was sealed with a rubber septum, vented by a needle, and stirred in a 70 °C oil bath for 48 h. After standing at room temperature overnight, the reaction mixture was suction filtered
through a fine porosity glass frit and the matte blue precipitate washed with 10 mL methanol. The precipitate was dissolved in 10 mL chloroform and the solution gravity filtered through filter paper to remove unreacted lead acetate. The filtrate was evaporated on a rotary evaporator and the solid slurried in acetonitrile, then suction filtered to give 153.4 mg of Pb(DOPO\(^2\))\(_2\) (44%). \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 1.19, 1.44 (s, 36H each, \(^7\)Bu), 7.46 (s, 4H, Ar\(\text{H}\)). \(^{13}\)C\{\(^1\)H\} NMR (CDCl\(_3\)): \(\delta\) 29.10, 30.33 (C(CH\(_3\))\(_3\)), 33.95, 34.98 (C(CH\(_3\))\(_3\)), 119.40 (aromatic CH), 133.86, 136.22, 137.60, 143.41, 173.78 (COPb). IR (cm\(^{-1}\)): 2954 (w), 2910 (w), 2867 (w), 1614 (w), 1589 (w), 1577 (m), 1510 (m), 1491 (m), 1453 (m), 1393 (m), 1384 (w), 1360 (m), 1350 (s), 1335 (m), 1325 (m), 1279 (m), 1245 (m), 1229 (m), 1205 (m), 1193 (m), 1166 (m), 1082 (m), 1071 (m), 1033 (m), 1021 (w), 998 (s), 982 (m), 928 (w), 908 (w), 898 (w), 876 (m), 806 (w), 791 (w), 779 (w), 774 (w), 740 (m), 731 (w), 698 (m), 659 (w), 614 (m), 602 (w), 596 (w), 545 (w), 530 (w), 516 (w), 510 (m). UV-Vis (CH\(_2\)Cl\(_2\)): \(\lambda_{\text{max}} = 254\) nm (\(\varepsilon = 31700\) M\(^{-1}\)cm\(^{-1}\)), 299 nm (21500 M\(^{-1}\)cm\(^{-1}\)), 402 nm (21100 M\(^{-1}\)cm\(^{-1}\)), 708 nm (16400 M\(^{-1}\)cm\(^{-1}\)). ESI-MS: 1081.5530 (M + H, calcd 1081.5550). Anal. Calcd for C\(_{56}\)H\(_{78}\)N\(_2\)O\(_6\)Pb: C, 62.25; H, 7.09; N, 2.59. Found: C, 62.05; H, 7.00; N, 2.59.

**Bis(2,4,6,8-tetra-tert-butyl-1,9-dioxophenoxazinato)chromium(III), Cr(DOPO)\(_2\).** In the drybox, 54.4 mg chromocene (Strem, 0.299 mmol) and 251.2 mg H(DOPO\(^2\)) (1.92 equiv) were weighed into a 20 mL scintillation vial and dissolved in 4 mL toluene. The vial was capped and allowed to stir overnight at room temperature. The sample was taken out of the drybox and the solvent removed on a rotary evaporator. The solid residue was slurried in 20 mL acetonitrile before suction filtration through a fine porosity glass frit to yield Cr(DOPO)\(_2\), 220 mg. The crude product was dissolved in 4 mL
benzene and layered with 8 mL acetonitrile. Dark green crystals were harvested after 24 h and washed with 10 mL acetonitrile to recover 160.5 mg (60%). $^1$H NMR (CDCl$_3$): $\delta$ 1.38 (br, 36H, tBu), 2.60 (br s, 36H, tBu), 49.27 (v br s, 4H, ArH). IR (cm$^{-1}$): 2956 (w), 2910 (w), 2869 (w), 1608 (w), 1584 (w), 1538 (w), 1528 (m), 1498 (m), 1481 (w), 1468 (w), 1428 (w), 1405 (m), 1387 (w), 1359 (w), 1350 (w), 1333 (w), 1309 (m), 1285 (m), 1248 (m), 1194 (w), 1158 (w), 1089 (m), 1068 (w), 1052 (w), 1042 (m), 1024 (w), 1010 (m), 927 (w), 908 (w), 876 (m), 826 (w), 794 (w), 777 (w), 761 (w), 745 (w), 716 (w), 695 (m), 668 (w), 657 (w), 646 (w), 640 (w), 618 (w), 609 (w), 598 (w), 586 (w), 581 (w), 576 (w), 568 (w), 561 (w), 556 (w), 552 (w), 545 (w), 539 (w), 525 (m), 519 (m), 511 (m), 505 (s). UV-Vis (CH$_2$Cl$_2$): $\lambda_{max} = 255$ nm (e = 32800 M$^{-1}$cm$^{-1}$), 279 nm (sh, 26200 M$^{-1}$cm$^{-1}$), 362 nm (17400 M$^{-1}$cm$^{-1}$), 416 nm (23100 M$^{-1}$cm$^{-1}$), 539 nm (4000 M$^{-1}$cm$^{-1}$), 688 nm (8100 M$^{-1}$cm$^{-1}$), 765 nm (sh, 6000 M$^{-1}$cm$^{-1}$). ESI-MS: 924.4927 (M$^+$, calcld 924.5110). Anal. Calcd for C$_{56}$H$_{76}$N$_2$O$_6$Cr: C, 72.70; H, 8.28; N, 3.03. Found: C, 69.72; H, 8.09; N, 2.73.

**Bis(2,4,6,8-tetra-tert-butyl-1,9-dioxophenoxazinato)tungsten(VI),**

W(DOPO$^{Cat}$)$_2$. In the drybox, 64.1 mg W$_2$Br$_4$(CO)$_8$ (0.070 mmol) and 153.4 mg Pb(DOPO$^{O}$)$_2$ (0.142 mmol, 1.01 mol per mol W) were weighed into a 20 mL scintillation vial and dissolved in 4 mL chloroform. Immediate carbon monoxide evolution was observed. The vial was capped and the reaction mixture stirred overnight at room temperature. The reaction mixture was then gravity filtered in the air and the filtrate evaporated to dryness on the rotary evaporator. The brown residue was triturated with acetonitrile and suction filtered on a fine porosity glass frit to recover W(DOPO$^{Cat}$)$_2$ as an amber brown solid, 123.9 mg (72%). $^1$H NMR (CDCl$_3$): $\delta$ 1.28, 1.48 (s, 36H each, tBu),...
6.47 (s, 4H, ArH). $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 29.44, 30.56 (C(CH$_3$)$_3$), 34.64, 34.68 (C(CH$_3$)$_3$), 124.57 (aromatic CH), 126.62, 128.46, 131.27, 141.94, 164.26 (COW). IR (cm$^{-1}$): 2953 (m), 2917 (w), 2869 (w), 1591 (w), 1499 (w), 1477 (w), 1457 (m), 1392 (w), 1362 (w), 1331 (w), 1305 (w), 1256 (w), 1234 (m), 1217 (m), 1175 (w), 1071 (s), 1031 (m), 1019 (m), 906 (w), 869 (w), 825 (w), 768 (m), 758 (m), 723 (w), 704 (m), 654 (m), 622 (w), 608 (w), 580 (m), 547 (s), 540 (s), 527 (m), 507 (s). UV-Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ = 412 nm (43500 M$^{-1}$cm$^{-1}$), 469 nm (sh, 16100 M$^{-1}$cm$^{-1}$). Anal. Calcd for C$_{56}$H$_{76}$N$_2$O$_6$W: C, 63.63; H, 7.25; N, 2.65. Found: C, 61.98; H, 6.99; N, 2.41.

**Bis(2,4,6,8-tetra-tert-butyl-1,9-dioxophenoxazinato)molybdenum(VI),**

Mo(DOPO$^{\text{Cat}}$)$_2$. Using the same procedure as for the tungsten analogue, 70.7 mg Mo$_2$Br$_4$(CO)$_8$ (0.096 mmol) and 203.8 mg Pb(DOPO$^{\text{Q}}$)$_2$ (0.189 mmol, 0.98 mol per mol Mo) were reacted in chloroform. The reaction mixture was allowed to stir for 2 h at room temperature before workup. Mo(DOPO$^{\text{Cat}}$)$_2$ was isolated as a deep brown solid, 111.3 mg (61%). $^1$H NMR (CDCl$_3$): $\delta$ 1.33, 1.45 (s, 36H each, 'Bu), 6.62 (s, 4H, ArH). $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 29.58, 30.60 (C(CH$_3$)$_3$), 34.56, 34.82 (C(CH$_3$)$_3$), 127.12 (aromatic CH), 127.80, 128.13, 132.25, 140.15, 168.29 (COMo). IR (cm$^{-1}$): 2953 (m), 2918 (w), 2868 (w), 1744 (w), 1621 (w), 1578 (w), 1546 (w), 1497 (w), 1479 (w), 1449 (w), 1392 (w), 1362 (w), 1331 (w), 1302 (w), 1255 (w), 1238 (m), 1217 (m), 1176 (w), 1071 (s), 1037 (m), 1018 (w), 929 (w), 906 (w), 875 (m), 829 (w), 789 (w), 768 (m), 749 (w), 716 (w), 701 (m), 641 (m), 625 (m), 607 (w), 577 (m), 540 (s), 505 (s). UV-Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ = 312 nm ($\epsilon$ = 12000 M$^{-1}$cm$^{-1}$), 463 nm (62800 M$^{-1}$cm$^{-1}$), 605 (6500 M$^{-1}$cm$^{-1}$). ESI-MS: 971.4806 (M + H, calcd 971.4836). Anal. Calcd for C$_{56}$H$_{76}$N$_2$O$_6$Mo: C, 69.33; H, 8.00; N, 2.89. Found: C, 66.60; H, 7.75; N, 2.70.

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Bis(2,4,6,8-tetra-tert-butyl-1,9-dioxophenoxazinato)dioxomolybdenum(VI),

MoO$_2$(DOPO$^0$)$_2$. In the drybox, 131.4 mg MoO$_2$Cl$_2$(dmf)$_2$ (0.381 mmol) and 324.4 mg Pb(DOPO$^0$)$_2$ (0.79 equiv) were weighed into a 20 mL scintillation vial and dissolved in 5 mL chloroform. The vial was capped and allowed to stir for 24 h. The reaction mixture was filtered through a fine porosity glass frit to remove PbCl$_2$. Solvent was evaporated on the vacuum line, leaving an oily dark blue residue that hardened into a glass. The product was triturated with acetonitrile, then filtered through a fine porosity glass frit, to recover 264.5 mg of MoO$_2$(DOPO$^0$)$_2$. The crude product was dissolved in 2 mL dichloromethane and layered with 8 mL acetonitrile. After 3 days in the -20 °C freezer, crystals were harvested and washed with minimal acetonitrile to recover 244.5 mg (81%). $^1$H NMR (CDCl$_3$): δ 0.96, 1.42, 1.43, 1.50 (s, 9H each, tBu), 7.33, 7.53 (s, 2H each, ArH).

X-ray Crystallography. On the benchtop, crystals of Pb(DOPO)$_2$•2C$_6$H$_6$ were grown by vapor diffusion of methanol into a benzene solution of the complex while the Cr(DOPO)$_2$ crystals were grown by vapor diffusion of acetonitrile into chloroform. Crystals of W(DOPO)$_2$ and Mo(DOPO)$_2$ were grown using the same recrystallization procedure as Cr(DOPO)$_2$ but in inert atmosphere. Crystals were coated in fluorinated polyether oil and placed onto a nylon loop before being mounted onto a Bruker Apex II CCD diffractometer under a cold N$_2$ stream.

Absorption correction was applied for all structures using the SADABS program. The structure of Pb(DOPO)$_2$•2C$_6$H$_6$ was solved using the Patterson method. The structures of Cr(DOPO)$_2$ and W(DOPO)$_2$ were solved by direct methods, while the model derived from W(DOPO)$_2$ was used to solve the structure of the isomorphous Mo(DOPO)$_2$.
crystal. All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Calculations used SHELXTL (Bruker AXS).\textsuperscript{23}

Vapor diffusion of acetonitrile into a dichloromethane solution of MoO\textsubscript{2}(DOPO)\textsubscript{2} in the drybox yielded crystals that were of poor quality for x-ray crystallography. The few single crystals were small and diffracted weakly. There was no good high angle data; reflections were measured only until 0.8 Å resolution, and, upon data processing and refinement, reflections below 1.0 Å resolution were omitted. Reflections were corrected for absorption by multi-scan methods. The structure was solved using direct methods. All nonhydrogen atoms were refined anisotropically. One atom, C45, could not be refined anisotropically in an unconstrained refinement, so its thermal parameters were restrained to be approximately isotropic with an esd of 0.002 using the ISOR command in SHELX. All hydrogen atoms were placed in calculated positions.

**Magnetic Susceptibility Measurements in Solution.** In the drybox, 40.0 mg of dimethyl terephthalate was dissolved in deuterated toluene, giving a total weight of 1.5047 g. 8.7 mg of Cr(DOPO)\textsubscript{2} was dissolved in this toluene solution with a total mass of 0.9788 g. The analyte solution was transferred into a sealable NMR tube while the remaining toluene solution was pipetted into a coaxial insert. The insert was placed inside the NMR tube before sealing with a Teflon-lined cap. Variable temperature NMR spectra were taken using a Varian VXR-500. Shifts in the resonances of dimethyl terephthalate peaks, in the absence and presence of Cr(DOPO)\textsubscript{2} in solution, were measured in hertz (Hz). For magnetic susceptibility calculations,\textsuperscript{24} analyte concentration has been corrected to take into account the thermal expansion of deuterated toluene. Values for the density of toluene in varying temperatures were taken from the literature.\textsuperscript{25}
Solid State Magnetic Susceptibility Measurement. 19.05 mg of Cr(DOPO)$_2$ was weighed onto a 16.0 mg 2 x 2 cm piece of Parafilm. The Parafilm was folded several times over to form a small pellet, taking care to prevent air bubbles. The pellet was put into one half of a gel capsule. The other half of the capsule was packed tightly coaxially on top of the sample. The capsule was inserted into a straw, tethered in place an inch from the end by poking holes above and below where the capsule should sit. The magnetic susceptibility ($\chi_{\text{meas}}$) of the sample in varying temperatures was measured using a Quantum Design Magnetic Property Measurement System (MPMS). To calculate for the paramagnetic component ($\chi_P$),$^{26}$ contributions from the diamagnetic elements ($\chi_D$) were subtracted. $\chi_D$ was derived from the following (Equation 3):

$$X_D = kM \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \tag{Eq. 3}$$

where $M$ is the molecular weight of the compound and $k = 0.45^{26a}$ for paramagnetic compounds of low molecular weight. Contributions from the sample holder were excluded by measuring the magnetic susceptibility of the Parafilm and gel capsule together, and subtracting it from $\chi_{\text{meas}}$.

2.3 Results

Synthesis of Group VI M(DOPO)$_2$ Complexes. In 2009, Minkin and coworkers reported the preparation of H(DOPO$^0$). 2,6-Dihydroxy-3,5-di-tert-butylaniline was prepared successfully according to this literature procedure$^8$ (Figure 8). However, refluxing aniline with 3,5-di-tert-butylcatechol in benzene using a catalytic amount of toluenesulfonic acid yielded no product. Replacing the catalyst with 10 mol% triethylamine and conducting the reaction in air at room temperature allowed for the
formation of HDOPO, albeit in modest yields (~25%). One of the challenges of this synthesis is the limited stability of the aniline in air. It oxidizes readily, the white chalky substance turning slightly purple just seconds after workup. Hence, the aniline was dried overnight in the drybox antechamber before storage in the drybox. Traces of phenoxazinone were observed in the NMR spectra, evidence of a side reaction that is depleting aniline and exacerbating poor yields. Remaining starting material and byproducts were easily removed by a simple trituration of the crude product in methanol, giving purple crystalline HDOPO.

![Chemical structure and reaction conditions](image)

**Figure 8.** Synthesis of H(DOPO$^0$)

The reaction mechanism for the last step remains unclear. It can be postulated that the base catalyzes the tautomerization of catechol (Figure 9). The condensation of aniline with di-tert-butylcatechol links the two rings followed by oxidation. At this point, the intermediate looks remarkably similar to ONO with a hydroxyl group at the C6 position of the phenol ring. It cyclizes to form an oxygen bridge between the two rings followed by another oxidation to form H(DOPO$^0$). Alternatively, a second condensation reaction can occur, forming phenoxazinone.
Reaction of aniline and di-\textit{tert}-butylcatechol with triethylamine in inert or oxygen-deficient atmosphere (such as in a capped NMR tube or 20 mL scintillation vial) yielded no reaction. No intermediates were observed in the NMR spectra even after refluxing for seven days. This suggests that the condensation reaction is reversible and that the driving force towards the formation of H(DOPO\textsuperscript{O}) is the oxidation of the linked rings. Hence, the reaction was conducted in air to ensure ample concentration of O\textsubscript{2} in solution.

Still, there is much to be improved on the preparation of H(DOPO\textsuperscript{O}). Increasing the reaction rate may improve the yield, as the conversion of aniline to H(DOPO\textsuperscript{O}) will be faster than its rate of decomposition. One way to accelerate the reaction is by increasing temperature. However, the refluxing of aniline and di-\textit{tert}-butylcatechol with triethylamine in benzene in a capped 20 mL vial yielded no product and showed

\textbf{Figure 9.} Proposed mechanism for the synthesis of H(DOPO\textsuperscript{O}) and the formation of the side product, Phenoxxazinone
decomposition of starting materials. This experiment has not been conducted out in the air. Another strategy is to conduct the reaction in an oxygen-rich environment. If oxidation of the linked rings is really an essential step in the formation of H(DOPO)

then the reaction rate should be dependent on the concentration of O2. Oxygen gas was bubbled into a benzene solution of aniline and di-tert-butylcatechol with triethylamine for 10 mins. The 25 mL round bottom flask containing the reaction mixture was covered with a rubber septum, purged with O2, and stirred at room temperature overnight. The reaction yielded no product, and, although aniline was still present in solution, the di-tert-butylcatechol had decomposed.

Cr(DOPO)2 was prepared from the reaction of 2 equiv of HDOPO with chromocene in benzene or toluene (Equation 4). The reaction was conducted in the drybox since chromocene, much like all Cr(II) compounds, oxidizes readily. Cr(DOPO)2 has limited solubility in benzene and toluene and, therefore, readily precipitates out of solution. Still, trituration of the crude product with acetonitrile improved the recovery of the product (60%).

\[
\text{Cp}_2\text{Cr} + 2 \text{H(DOPO)}\overset{\text{Toluene}}{\longrightarrow} \text{Cr(DOPO)}_2 + 2 \text{CpH} \quad (\text{Eq. 4})
\]

\[
\text{Pb(OAc)}_2 + 2 \text{H(DOPO)} \overset{\text{MeOH}}{\longrightarrow} \text{Pb(DOPO)}_2 + 2 \text{HOAc} \quad (\text{Eq. 5})
\]

Pb(ONO)2 has been proven to be an effective reagent for the replacement of halides with the ONO ligand in transition metal complexes.27 A similar strategy was employed for the synthesis of the remaining group VI metal complexes. To form Pb(DOPO)2, a solution of lead acetate trihydrate, Pb(OAc)2•3H2O, and two equiv of
HDOPO in methanol was heated overnight (Equation 5). Pb(DOPO)₂ is insoluble in cold methanol and precipitates, albeit slowly, from the reaction mixture as a fine blue powder. The yields are decent (~44%) but the procedure does not scale up well due to the poor solubility of lead acetate trihydrate in most organic solvents. Large volumes, roughly 1 mL of methanol per mg of Pb(OAc)₂•3H₂O, have to be used as well as longer reaction times. The workup also needs to be more efficient. Precipitation of Pb(DOPO)₂ in such low concentrations slows the process. In fact, low yields are primarily due to low recovery of product from the reaction mixture. One could try a two-phase reaction with Pb(OAc)₂•3H₂O in water and HDOPO in chloroform. Mixing the two layers would allow the reagents to interact; Pb(DOPO)₂ along with other byproducts such as acetic acid will go to the organic layer while unreacted lead acetate trihydrate will stay in the aqueous layer. In an alternative procedure, an organic-soluble Pb(II) precursor, lead 2-ethylhexanoate, was employed. The procedure gives higher yields (80%) and works well on a gram scale with the only problem being that lead 2-ethylhexanoate is difficult to handle.

The crystal structure of Pb(DOPO)₂ illustrates κ²-like coordination of the DOPO ligands to Pb with each ligand having one short Pb-O bond (Pb–O = 2.319(11) Å avg) and one long Pb-O bond (Pb–O = 2.78(3) Å avg.) (Figure 10). It has a hemi-directed geometry, that is, occupants of the first coordination sphere are only distributed in a limited part of the globe, leaving a void. This is due to the lone pair of electrons in the 6s orbital of Pb(II), made stereochemically active by the contribution of some p character from the 6p bonding orbital. AX₄E complexes, where A is the central atom, X is the ligand, and E is the lone pair, have a trigonal bipyramidal geometry, with the lone pair of
electrons in the equatorial plane.\textsuperscript{30} Pb(DOPO)\textsubscript{2} adopts this configuration with the nitrogens in an equatorial orientation and the oxygens in an axial orientation, albeit slightly bent (O–Pb–O < 90\degree).

Figure 10. Thermal ellipsoid plot of Pb(DOPO)\textsubscript{2}

The asymmetry in the coordination of each ring to the metal center can also be observed within the ligand. By compiling a database of amidophenoxide structures with unambiguous oxidation states, Brown developed a simple linear regression model correlating intraligand bond lengths with oxidation states.\textsuperscript{31} Due to the abundance of M(ONO)\textsubscript{2} complexes in literature, there was enough data to allow for the parameterization of ONO ligands.\textsuperscript{28} This model was used to calculate the metrical oxidation state (MOS) of DOPO ligands from their observed bond lengths. Note, however, that there may be some systematic variations because of the polycyclic nature
of the DOPO ligand and heteroatom substitution. For each DOPO ligand, the ring that
binds weakly to Pb is less negative than the other (MOS_{ave} = -0.5 vs. MOS_{ave} = -1.6).
This is consistent with the ligand being in its quinonoid form; the oxo ring coordinates
weakly with the metal center while the phenoxide ring forms a stronger bond with Pb.
Variable temperature experiments showed that the structure is highly fluxional in
solution, with symmetrical spectra (only one aromatic signal and two 'Bu signals) for
down to -60 °C.

\[
Pb(\text{DOPO})_2 + 1/2 \text{M}_2\text{Br}_4(\text{CO})_8 \xrightarrow{\text{CHCl}_3, \text{r.t.} 2 \text{ hrs}} \text{M}(\text{DOPO})_2 + \text{PbBr}_2 + 4 \text{ CO} \quad (\text{Eq. 6})
\]

\[
\text{M} = \text{W} \quad 72\%
\text{Mo} \quad 61\%
\]

W(\text{DOPO})_2 and Mo(\text{DOPO})_2 were prepared by reacting 2 equiv of Pb(\text{DOPO})_2
with \text{W}_2\text{Br}_4(\text{CO})_8 and \text{Mo}_2\text{Br}_4(\text{CO})_8 in chloroform, respectively (Equation 6). This was
conducted in the drybox, as both the tungsten and molybdenum complexes are air
sensitive. On the other hand, their corresponding products can survive in the air for a few
hours. Workup is done on the benchtop where the reaction mixture is filtered, then
evaporated to dryness and triturated with acetonitrile to give W(\text{DOPO})_2 (72%) and
Mo(\text{DOPO})_2 (61%) in good yields. The driving force of the reaction is the formation of
\text{PbBr}_2, which precipitates readily in organic solvents such as chloroform. The problem
lies in its removal as \text{PbBr}_2 still remains even after multiple recrystallization attempts and
gravity filtration over paper. It has been recently determined that the compounds could
survive column chromatography. The compounds were run through a short plug of silica
gel and eluted with methylene chloride. After evaporating off the solvent, they were
triturated with acetonitrile and filtered to give analytically pure samples.\(^{28}\)
Characterization of Group VI M(DOPO)$_2$ Complexes. The crystal structures show that W(DOPO)$_2$ and Mo(DOPO)$_2$ are isomorphous to each other, as well as to Fe(DOPO)$_2$. The DOPO ligands coordinate to the metal centers in a meridional fashion, forming a distorted octahedral geometry (Figure 11 and 12). Both metal complexes have approximate (i.e. noncrystallographic) $D_{2d}$ symmetry but Mo(DOPO)$_2$ shows slightly shorter M-N bonds than W(DOPO)$_2$ (Appendix III). This suggests a stronger more covalent bond, and is plausible, considering that Mo is more electronegative than W. Its d orbitals are lower in energy than that of W, and, therefore, can mix better with the HOMO of the DOPO ligand.

Figure 11. Thermal ellipsoid plot of W(DOPO)$_2$
Figure 12. Thermal ellipsoid plot of Mo(DOPO)$_2$

The average metrical oxidation states of the DOPO ligands in W(DOPO)$_2$ and Mo(DOPO)$_2$ are -3.0 and -2.8, respectively. The ligands are in their fully reduced form, and the metals are formally +6. The change in oxidation state can be observed by NMR for both metal complexes, where one sees a $\sim$1 ppm upfield shift for the ring proton in the $^1$H spectra and a $\sim$10 ppm upfield shift for the coordinating C-O carbon in the $^{13}$C spectra relative to Pb(DOPO)$_2$. Interpreting the $^{13}$C NMR spectra is straightforward; the resonance shifts upfield as the carbon environment changes from a deshielded pseudo $\alpha$, $\beta$ – unsaturated carbonyl carbon of DOPO$^0$ to a shielded phenoxide carbon of DOPO$^\text{Cat}$. Although the protons of the DOPO ligand experience the same changes in environment, this does not explain the drastic shift in the $^1$H NMR spectra, as the same phenomenon is not observed in the case of their corresponding M(ONO)$_2$ analogues. The chemical shift
in the $^1$H NMR spectra is attributed to ring current effects. Aromatic protons experience diatropic ring currents that flow in the same direction as the external magnetic field. This has a deshielding effect on outer protons. Conversely, antiaromatic protons experience paratropic ring currents, which flow in the opposite direction as the external magnetic field and have a shielding effect. When the DOPO ligand gets reduced by two electrons, it becomes formally antiaromatic, and the ring proton is shielded by paratropic ring currents.

The oxidation states of W and Mo are well defined; the energies of their d orbitals are significantly higher than the HOMO of the DOPO ligand, thus, the orbitals participating in multielectron transfer reactions are predominantly ligand in character. This is not the case for Cr, which is the most electronegative of the three group VI transition metals. Its d orbitals are low enough in energy to have significant mixing with the frontier orbitals of DOPO. In this case, it is not clear which percentage of the occupied $\pi$ bonding orbitals are metal in character or ligand in character. Hence, the oxidation states of the metal and ligands are ambiguous. The $^1$H NMR spectra show broad peaks and extreme shifts in resonances (arom. H normally located at 7.45 ppm was found at 49.27 ppm), indicative of a paramagnetic compound.

The crystal structure of Cr(DOPO)$_2$ shows meridional coordination of the DOPO ligands to Cr (Figure 13). However, unlike the other group VI metal complexes, there is a significant difference between the bonding of each DOPO ligand to the metal center. One of the DOPO ligands has shorter Cr-O and Cr-N bonds (Appendix III); MOS calculations show a partially reduced oxidation state (MOS$_{ave}$ = -2.3), both indicative of a more covalent bonding. The other ligand is in its oxidized form (MOS$_{ave}$ = -1.4) and maintains
a more ionic bonding. Since one ligand is closer to Cr than the other, symmetry devolves to $C_{2v}$. Cr is formally +3, with one ligand as DOPO$^{SO}$ and the other DOPO$^{O}$.

![Diagram of Cr(DOPO)$_2$](image)

**Figure 13.** Thermal ellipsoid plot of Cr(DOPO)$_2$

An octahedral Cr(III) species would be attracted to an applied magnetic field. The magnetic susceptibility of Cr(DOPO)$_2$ was measured in both solid and solution form. In solution, the compound exhibited Curie-Weiss paramagnetism, which is consistent with a triplet state (Figure 14). The Cr(DOPO)$_2$ solid behaves similarly but the slight slope in the $\chi T$ vs. $T$ graph (it should be constant for temperature dependent paramagnetism) may be due to some impurities in the sample or some temperature independent paramagnetism (Figure 15).
Figure 14. $\chi_{\text{mol}}$ of Cr(DOPO)$_2$ in solution decreases as temperature increases (top) while $\chi_{\text{mol}}T$ stays constant (bottom). This is consistent with Curie-Weiss Paramagnetism.
Figure 15. $\chi_{\text{mol}}$ of Cr(DOPO)$_2$ solid decreases with increasing temperature (top) but $\chi_{\text{mol}}T$ has a slight slope (bottom). There may be a mixture of temperature dependent and independent paramagnetism in the sample.
Reactivity of Group VI Metal Complexes. The reactivity of W(DOPO\textsuperscript{Cat})\textsubscript{2} and Mo(DOPO\textsuperscript{Cat})\textsubscript{2} in non-classical oxygenation reactions was probed using \textit{N}-oxides. A standard, dimethyl terephthalate, was employed in determining the stoichiometry of each reaction. The reaction of excess \textit{N}-methyl morpholine \textit{N}-oxide (NMO) with W(DOPO\textsuperscript{Cat})\textsubscript{2} yielded 1 equiv of H(DOPO\textsuperscript{Q}). All of the W(DOPO\textsuperscript{Cat})\textsubscript{2} was consumed, and 1.5 equiv of NMO was converted into \textit{N}-methyl morpholine (NMM). NMO is a two-electron oxidant, therefore, one of the ligands must have been fully oxidized (as is the case with H(DOPO\textsuperscript{Q})) while the other was partially oxidized, giving DOPO\textsuperscript{SQ}. We can then postulate the formation of a new metal complex containing a partially oxidized ligand, WO\textsubscript{2}(DOPO\textsuperscript{SQ}) (Equation 7). Note that to balance the equation, trace amounts of water must be present in solution.

\[
\text{M(DOPO}^{\text{Cat}}\text{)}_2 + 1.5 \text{ NMO} + 0.5 \text{ H}_2\text{O} \xrightarrow{\text{CDCl}_3} \text{MO}_2(\text{DOPO}^{\text{SQ}}) + 1.5 \text{ NMM} + \text{H(DOPO}^{\text{Q}}) \quad (\text{Eq. 7})
\]

WO\textsubscript{2}(DOPO\textsuperscript{SQ}) has an odd number of electrons and, consequently, is paramagnetic. This explains why no new product peaks were observed in the \textsuperscript{1}H spectra despite the full consumption of the starting material; the paramagnetic compound is NMR-silent. Over time, the H(DOPO\textsuperscript{Q}) peaks grew in; 2 equiv of H(DOPO\textsuperscript{Q}) was recovered, and clear solid (WO\textsubscript{3}) could be found on the bottom of the NMR tube. WO\textsubscript{2}(DOPO\textsuperscript{SQ}) seems to decompose in the presence of excess oxidant, making it difficult to isolate from solution. To determine its structure, the paramagnetic compound would need to be prepared independently.

Analogous experiments using Mo(DOPO\textsuperscript{Cat})\textsubscript{2} as a starting material yielded similar results, albeit at a slower rate. This is plausible since W is less electronegative, and, therefore more reducing than Mo. More importantly, a new set of peaks appeared in the
NMR spectra (40%). Two singlets with equal intensity were observed at 7.30 and 7.51 ppm. Two more singlets can be seen at 0.93 and 1.39 ppm. The peak at 0.93 ppm integrates to half of the peak at 1.39 ppm. It is possible that the downfield peak is actually made up of two inequivalent peaks with very similar resonances (exacerbated by the presence of excess NMO in solution that can lead to line broadening and significant shifts), and that the aliphatic peaks belong to three \(^{1}\text{Bu}\) groups in a set of four. The fourth \(^{1}\text{Bu}\) group was later found under one of the \(^{3}\text{Bu}\) groups of H(DOPO\(^{O}\)) at 1.47 ppm.

Figure 16. Predicted structure of MoO\(_2\)(DOPO\(^{O}\))\(_2\)

This pattern, 2 arom. H and 4 \(^{1}\text{Bu}\) groups, suggests a loss of symmetry which is consistent with the predicted MO\(_2\)(DOPO\(^{O}\))\(_2\) structure (M = W or Mo). Based on the structures of most dioxo metal(VI) complexes in literature, the product would be expected to retain its distorted octahedral geometry, with the oxo groups in a cis configuration to maximize \(\pi\) bonding, and the nitrogens opposite the oxo groups due to the oxo’s trans-directing effect\(^{32}\) (Figure 16). To achieve this geometry, the DOPO ligands would have to adopt a \(\kappa^2\) coordination to the metal center with the more oxidized ring detached. In this structure, the DOPO ligand would be totally unsymmetrical, both aromatic hydrogens and all \(^{1}\text{Bu}\) groups would be distinct from each other. However, the
two DOPO ligands may be interchangeable by a two-fold symmetry that bisects the plane containing the two oxo groups and the two nitrogens.

To prevent the formation of the paramagnetic compound, MO₂(DOPO\textsuperscript{SQ})\textsubscript{2}, NMO was replaced with a stronger oxidant to hopefully accelerate the reaction time, minimizing the possibility of side reactions. The reaction of excess trimethylamine N-oxide, Me₃NO, with Mo(DOPO\textsuperscript{Cat})\textsubscript{2} afforded the new product MoO₂(DOPO\textsuperscript{Q})\textsubscript{2} (90\%) (Equation 8). Approximately 2 equiv of Me₃NO was converted to trimethylamine, Me₃N, and any discrepancy can be attributed to the formation of trace amounts of H(DOPO\textsuperscript{Q}) and, therefore, paramagnetic compound. Nevertheless, the presence of these impurities would make it difficult to isolate the product from solution. A similar reaction using W(DOPO\textsuperscript{Cat})\textsubscript{2} as the starting material gave the new compound as a major product (71\%) (\textsuperscript{1}H (CDCl\textsubscript{3}): δ 0.93, 1.40, 1.42, 1.49 (s, 18H each, \textsuperscript{t}Bu) 7.38, 7.60 (s, 2H, ArH)).

\[
\text{M(DOPO}^{\text{Cat}}\text{)}\textsubscript{2} + 2 \text{Me}_{3}\text{NO} \xrightarrow{\text{CDCl}_{3}} \text{MO}_{2}\text{(DOPO}^{Q}\text{)}\textsubscript{2} + 2 \text{Me}_{3}\text{N} \quad (\text{Eq. 8})
\]

The reaction of M(DOPO\textsuperscript{Cat})\textsubscript{2} (M = Mo, W) with the first equivalent of oxidant is facile. It forms a transient intermediate MO(DOPO\textsuperscript{SQ})\textsubscript{2}. Reaction of a second equivalent gives MO₂(DOPO\textsuperscript{Q})\textsubscript{2}. However, if the second oxidation is not fast enough (i.e. the oxidant is not very reactive) and trace amounts of water are present in solution, paramagnetic material, MO₂(DOPO\textsuperscript{SQ})\textsubscript{2}, may be produced.

**Synthesis and Characterization of MoO₂(DOPO\textsuperscript{Q})\textsubscript{2}**. To determine the structure of the new compound, MoO₂(DOPO\textsuperscript{Q})\textsubscript{2}, several attempts were made to synthesize it independently. Procedures using 2 equiv of H(DOPO\textsuperscript{Q}) with MoO₂(OSiPh\textsubscript{3})\textsubscript{2} or MoO₂(acac)\textsubscript{2} were unsuccessful. The driving force for these reactions is the basicity of HOSiPh\textsubscript{3} (pK\textsubscript{a} ~ 11) and acacH (pK\textsubscript{a} ~ 9). Unfortunately, the pK\textsubscript{a} of H(DOPO\textsuperscript{Q}) has not
been determined precisely. We know that it is somewhere between 4.76-13.8, but H(DOPO)\(^0\) could very well be more or just as basic as HOSiPh\(_3\) and acacH. No reaction was observed in the case of MoO\(_2\)(acac)\(_2\). As for MoO\(_2\)(OSiPh\(_3\))\(_2\), unpredictable shifts in the resonances of both starting materials suggest hydrogen bonding between the H(DOPO)\(^0\) and OSiPh\(_3\) ligand but no dissociation of silanol from the metal center.

Instead, Pb(DOPO)\(^0\)\(_2\) was employed as a transfer agent to displace Cl from MoO\(_2\)Cl\(_2\)(dmf)\(_2\) and form MoO\(_2\)(DOPO)\(^0\)\(_2\) in moderate yields (81\%) (Equation 9). The reaction time needs to be optimized. After 24 h, traces of H(DOPO)\(^0\) from the hydrolysis of MoO\(_2\)(DOPO)\(^0\)\(_2\) can already be observed. Decreasing the reaction time may prevent product decomposition but the reaction rate is greatly hampered by the limited solubility of MoO\(_2\)Cl\(_2\)(dmf)\(_2\) in chloroform. Isolation and purification of MoO\(_2\)(DOPO)\(^0\)\(_2\) also needs to be improved. Unreacted MoO\(_2\)Cl\(_2\)(dmf)\(_2\) was filtered out of solution along with PbCl\(_2\). To attempt to remove H(DOPO)\(^0\), the crude product was triturated in acetonitrile. Unfortunately, MoO\(_2\)(DOPO)\(^0\)\(_2\) is slightly soluble in this solvent, consequently, some product is lost in this step. Most of the H(DOPO)\(^0\) was washed away but traces still remain. Hence, the product was further purified by recrystallization via the liquid diffusion of acetonitrile into dichloromethane. Crystals of MoO\(_2\)(DOPO)\(^0\)\(_2\) were only recovered when the process is slowed down by cooling in the -20°C freezer in the drybox.

\[
\text{MoO}_2\text{Cl}_2(\text{dmf})_2 + \text{Pb}(\text{DOPO})^0_2 \xrightarrow{\text{CDCl}_3} \text{MoO}_2(\text{DOPO})^0_2 + \text{PbCl}_2 + 2 \text{dmf} \quad (\text{Eq. 9})
\]

81%

The crystal structure of MoO\(_2\)(DOPO)\(^0\)\(_2\) differs significantly from the predicted distorted octahedral geometry. It forms an eight-coordinate dioxomolybdenum(VI)
complex, a novel structure according to a survey of the Cambridge Structural Database (Figure 17). The DOPO ligands have a $\kappa^3$ coordination to the metal center with long Mo-O and Mo-N distances (Mo-O$_{ave}$ = 2.252 and 2.314 Å Mo-N$_{ave}$ = 2.350 Å). The bonds may have been lengthened to prevent overcrowding about the metal center, to relieve oxygen-oxygen repulsions and to minimize the strain on the rigidly planar DOPO ligand. MoO$_2$(DOPO$^O$)$_2$ has a dodecahedral geometry, with two planes (each containing an oxo group and a DOPO ligand) perpendicular to each other. A similar procedure may be able to be used to prepare WO$_2$(DOPO$^O$)$_2$ independently, with Pb(DOPO$^O$)$_2$ displacing Cl in WO$_2$Cl$_2$dme (dme = dimethoxyethane).  

**Figure 17.** Thermal ellipsoid plot of MoO$_2$(DOPO$^O$)$_2$  

**Deoxygenation of MoO$_2$(DOPO$^O$)$_2$ to Give Mo(DOPO$^{Cat}$)$_2$.** To investigate the reactivity of MoO$_2$(DOPO$^O$)$_2$ in oxygen atom transfer reactions, it was reacted with 2 equiv of triphenylphosphine, PPh$_3$, and monitored by NMR. After 24 h, all starting
material had been consumed, PPh$_3$ converted into triphenylphosphine oxide, OPPh$_3$, and Mo(DOPO$^{\text{Cat}}$)$_2$ regenerated. One can clearly see that immediately after addition of PPh$_3$, almost half of the starting material has been consumed (Figure 18). However, only a very small amount of Mo(DOPO$^{\text{Cat}}$)$_2$ has been regenerated, hence, not all of MoO$_2$(DOPO$^O$)$_2$ has been accounted for. Concomitantly, a new set of peaks appeared at 1.05, 1.31, 1.38, 7.18 ppm and slightly downfield of 7.66 ppm. All of this suggests the formation of a PPh$_3$-containing intermediate. The unknown compound reaches its maximum accumulation at 2 h composing 20% of the total DOPO-containing compounds (with 1:2:2 ratio of PPh$_3$-containing intermediate to MoO$_2$(DOPO$^O$)$_2$ to Mo(DOPO$^{\text{Cat}}$)$_2$). At 5 h, there is twice the amount of PPh$_3$-containing intermediate compared to the bis(DOPO)-dioxomolybdenum compound.

\[
\text{MoO}_2\text{Cl}_2\text{dmf}_2 + \text{Pb(DOPO}^O\text{)}_2 \xrightarrow{\text{CHCl}_3 < 24 \text{ hrs}} \text{MoO}_2(\text{DOPO}^O)_2 \xrightarrow{2 \text{ PPh}_3} \text{Mo(DOPO}^{\text{Cat}}\text{)}_2 + 2 \text{ OPPh}_3
\]

**Figure 18.** Progression of the regeneration of Mo(DOPO$^{\text{Cat}}$)$_2$ from MoO$_2$(DOPO$^O$)$_2$
Determining the structure of an intermediate would be advantageous for future mechanistic studies. One useful experiment would be to monitor the reaction using $^{31}$P NMR. The absence of a phosphorus peak distinct from PPh$_3$ and OPPh$_3$ would rule out the possibility of a PPh$_3$-bound intermediate. Another easy experiment is to use deuterated PPh$_3$. This will eliminate the peaks corresponding to PPh$_3$ and OPPh$_3$ and clear up the aromatic region to find peaks corresponding to the DOPO ligands in the intermediate. Determining the symmetry from the $^1$H NMR spectra will allow us to predict a structure.

One possibility is that the intermediate contains bound OPPh$_3$. If so, a strategy to increase the lifetime of the intermediate is to slow down the dissociation of OP$R_3$ from the metal center. Basic phosphines and/or ones with less bulky substituents will form corresponding phosphine oxides that are more easily retained by the metal center.

Reacting 2 equiv of dimethylphenylphosphine, PMe$_2$Ph, with MoO$_2$(DOPO$^\text{Cat}$)$_2$ showed complete conversion to Mo(DOPO$^\text{Cat}$)$_2$ and OPMe$_2$Ph within 2 h. No intermediates were observed even at 30 min due to the fast reactivity of PMe$_2$Ph.

2.4 Conclusions

A modified procedure for the synthesis of H(DOPO$^\text{O}$) was developed using 10 mol percent triethylamine at room temperature in aerobic conditions. Cr(DOPO)$_2$ was prepared directly from the reaction of H(DOPO$^\text{O}$) with chromocene. Its crystal structure showed a significant difference in the binding of each DOPO ligand to Cr, with one ligand fully oxidized and the other partially reduced. The magnetic susceptibility of Cr(DOPO)$_2$ in solid and solution were measured. The compound exhibited weak
temperature dependent paramagnetism, consistent with a triplet state. However, the Cr(DOPO)$_2$ solid seems to exhibit temperature independent paramagnetism as well.

M(DOPO$^{\text{Cat}}$)$_2$ (M=Mo, W) have been synthesized by the displacement of halides in the corresponding metal precursors, M$_2$Br$_4$(CO)$_8$, using Pb(DOPO$^O$)$_2$. Their crystal structures showed similar geometries, with the DOPO ligands coordinating in a meridional fashion to the metal center. Mo formed slightly stronger bonds with the DOPO ligand than W but metrical oxidation calculations indicated that both compounds had fully reduced ligands. Reaction with N-oxides gave MO$_2$(DOPO$^O$)$_2$ but a weak oxidant and trace amounts of water lead to formation of a radical product, MO$_2$(DOPO$^{SO}$). Oxygen atom transfer from MoO$_2$(DOPO$^O$)$_2$ to phosphines regenerated Mo(DOPO$^{Cat}$)$_2$.

Further studies are needed to fully understand the non-classical oxygenation reactions of these group VI metal complexes. Identification of the paramagnetic intermediate may help prevent formation of radicals and make O$_2$ activation more efficient. The reactivity of MoO$_2$(DOPO$^O$)$_2$ with alkenes and alkynes has yet to be examined. Furthermore, it will be interesting to see if photolysis and thermolysis of MoO$_2$(DOPO$^O$)$_2$ can cause the evolution of O$_2$. Analogous studies may be conducted once WO$_2$(DOPO$^O$)$_2$ has been prepared.
CHAPTER 3
ENTEROBACTIN AND ITS REACTIVITY WITH MOLYBDENUM(VI)

3.1 Enterobactin

![Enterobactin diagram]

**Figure 19.** Model of Enterobactin bound to Fe(III). Figure from Ref. 35, reprinted by permission of the American Chemical Society.

Enterobactin is a siderophore produced by most gram-negative bacteria to sequester iron from their surroundings\(^\text{34}\) (Figure 19).\(^\text{35}\) Its structure and binding properties make it an excellent candidate for a redox-active ligand. Its 2,3-dihydroxybenzamide side chains are catechol groups, which have already been established as two electron donors. It should be noted, however, that the 2,3-dihydrobenzamide side chains are less electron-rich than catechol. Hence, the corresponding enterobactin-metal complex may not be as strong a reductant. Enterobactin has a hexadentate coordination with Fe(III), and is expected to bind in a similar fashion with group VI metals. This geometry may encourage formation of a seven- or eight-coordinate mono- or dioxo metal complex. High
coordination numbers can stabilize the peroxo intermediate. The geometry also leaves the top of the metal center open for substrate attack.

Enterobactin boasts one of the largest binding constants, $\log (K_{\text{bind}}) = 49$ for Fe(III), among natural compounds. Its success as an Fe(III) chelator is due the low conformational freedom in its free form and its low molecular strain upon coordinating to the metal center. This makes it more likely for the metal complex to retain the ligand within the coordination sphere even in its quinonoid form. The fact that group VI metal atoms are larger than Fe(III) should not affect the binding constants, as Fe-O and Mo-O bond lengths are very similar for metal-catecholate complexes. In the event that the 2,3-dihydroxybenzamide fails to exhibit redox-active properties, we can still utilize the trilactone scaffold and derivatize the side chains.

### 3.2 Experimental

Unless otherwise noted, all procedures were carried on the benchtop. When dry solvents were needed, chlorinated solvents and pyridine were dried over 4 Å molecular sieves, followed by CaH$_2$. Acetone was dried over 4 Å molecular sieves, and toluene was dried over sodium. Deuterated solvents were obtained from Cambridge Isotope Laboratories and dried using the same procedures as their protio analogues. All dry solvents were stored in the drybox prior to use. 2,2-Dibutyl-1,3-dioxa-2-stannolane was prepared using the method of Maillard and Deleuze. 2,3-Bis(benzyloxy)benzoic acid was prepared according to a literature procedure. All other reagents were commercially available and used without further purification. A Parr 3911 Shaker Hydrogenation Apparatus was used for the debenzylation of hexabenzylerobactin. Routine NMR
spectra were measured on CDCl$_3$ solutions on a Varian VXR-300. Chemical shifts for $^1$H and $^{13}$C{$^1$H} spectra are reported in ppm downfield of TMS, with spectra referenced using the chemical shifts of the solvent residuals.

**Tris(N-trityl-L-serine) Trilactone.** 5.0 g methyl N-trityl-L-serine methyl ester (Aldrich, 14.0 mmol) and 405.4 mg 2,2-dibutyl-1,3-dioxo-2-stannolane (0.1 equiv) were suspended in 150 mL toluene. The 500 mL round bottom flask containing the reaction mixture was equipped with a condenser and a Dean-Stark trap filled with 4 Å molecular sieves. The suspension was stirred vigorously at reflux under nitrogen for 3 days. After cooling to room temperature, the solvent was evaporated *in vacuo*, leaving a beige residue. The crude product was washed with methylene chloride to afford 3.5 g of white powder (74%). $^1$H NMR (CDCl$_3$, cf. lit.$^{35}$): $\delta$ 2.63 (d, $J''' = 10$ Hz, 3H, NH), 3.44 (dd, $J = 4.25$ Hz, $J' = 11$ Hz, 3H, H$_a$), 3.44 (ddd, $J = 4.25$ Hz, $J'' = 11$ Hz, $J''' = 10$ Hz, 3H, H$_b$), 4.05 (t, $J' = 11$ Hz, $J'' = 11$ Hz, 3H, H$_c$), 7.2-7.35 (m, 6H, trityl o-ArH), 7.4-7.5 (m, 9H, trityl p-ArH, m-ArH).

**2,3-Bis(benzyloxy)benzoyl Chloride.** In the drybox, 1.01 g 2,3-bis(benzyloxy)-benzoic acid (3.0 mmol) was weighed into a 50 mL round bottom flask. A stoichiometric amount of phosphorus pentachloride, PCl$_5$ (622.1 mg, 1 equiv), was added to the flask before dissolving the reagents in 10 mL toluene. The flask was sealed with a needle valve and was stirred at room temperature for 19 h. The solvent was evaporated on the vacuum line along with the resulting phosphoryl trichloride, POCl$_3$. 964.6 mg of product was recovered (91%) and stored in the -20 °C freezer in the drybox. $^1$H NMR (CDCl$_3$): $\delta$ 5.13, 5.17 (s, 2H each, -OCH$_2$(C$_6$H$_5$)), 7.1-7.6 (m, 13H, ArH and -OCH$_2$(C$_6$H$_5$)).
**Hexabenzylenterobactin.** In a 20 mL scintillation vial, 623.8 mg tris(N-trityl-L-serine) trilactone (0.631 mmol) and 780.2 mg 2,3-bis(benzyloxy)benzoyl chloride (3.5 equiv) were dissolved in 10 mL chloroform. The vial was capped and stirred at reflux for 7 h. After removing the solvent *in vacuo*, the crude product was purified via column chromatography. A 70:30 hexane/ethyl acetate solution was used to remove all the impurities then the silica column was flushed with neat ethyl acetate to recover pure product, 369.9 mg (49%). $^1$H NMR (CDCl$_3$): δ 4.03 (dd, $J' = 11$ Hz, $J'' = 7.5$ Hz, 3H, H$_c$), 4.17 (dd, $J = 4.5$ Hz, $J' = 11$ Hz, 3H, H$_a$), 4.93 (ddd, $J = 4.5$ Hz, $J'' = 7.5$ Hz, $J''' = 8$ Hz, 3H, H$_b$), 5-5.2 (m, 12H, -OCH$_2$(C$_6$H$_5$), 7.1-7.45 (m, 36H, p-ArH, m-ArH, and -OCH$_2$(C$_6$H$_5$), 7.65 (m, 3H, o-ArH), 8.5 (d, $J''' = 8$ Hz, 3H, NH).

**Enterobactin.** 149.9 mg hexabenzylenterobactin (0.124 mmol) and 69.5 mg 10% Pd/C were weighed into a 250 mL Parr reaction bottle. The reagents were dissolved in 20 mL of a 1:1 methanol/ethyl acetate solution. The reaction mixture was then hydrogenated at 60 psi for 24 h at room temperature. The catalyst was filtered off via gravity filtration on a glass funnel, plugged with cotton and lined with filter paper. The filter paper was washed with acetone, and the filtrate was evaporated to afford 76.8 mg of enterobactin (93%). $^1$H NMR ((CD$_3$)$_2$CO, cf. lit.$^{35}$): δ 4.68 (dd, $J' = 11$ Hz, $J'' = 7.5$ Hz, 3H, H$_c$), 4.76 (dd, $J = 4.5$ Hz, $J' = 11$ Hz, 3H, H$_a$), 5.12 (m, $J = 4.5$ Hz, $J'' = 7.5$ Hz, $J''' = 8$ Hz, 3H, H$_b$), 6.73 (t, 3H, m-ArH), 7.10 (dd, 3H, p-ArH) 7.34 (m, 3H, o-ArH).
3.3 Results

**Synthesis of Enterobactin.** The backbone of the enterobactin molecule was prepared using a procedure developed by Raymond and coworkers with slight modifications\(^9\) (Figure 20). 2,2-Dibutyl-1,3-dioxo-2-stannolane served as a template for the macrocyclization of \(N\)-trityl-\(L\)-serine methyl ester into a 12-membered trilactone ring. The purification method was simplified, foregoing column chromatography for a simple dichloromethane wash. Pure tris(\(N\)-trityl-\(L\)-serine) trilactone was recovered in moderate yields (74\%).

![Synthesis of Enterobactin](image)

**Figure 20.** Synthesis of Enterobactin
For the side chains, 2,3-bis(benzyloxy)benzoic acid was reacted with phosphorus pentachloride to form acyl chloride with excellent conversion (91%). The resulting phosphoryl trichloride, POCl₃, was evaporated off along with the solvent in the vacuum line. The crude product is used with no further purification so stoichiometric amounts of reagent should be used to prevent impurities. 2,3-Bis(benzyloxy)benzoyl chloride has a waxy texture. It degrades into an oily substance that is hard to handle, but it may be stored indefinitely at -20 °C.

Existing procedures on the preparation of benzyl-protected enterobactin require two separate steps: 1) removal of N-trityl protecting groups and 2) formation of the amide bond, linking the trilactone backbone with the side chains.⁴,⁹ Raymond and coworkers⁹ reported excellent yields for the deprotection step but reaction conditions were extremely harsh (0.4 M HCl solution in ethanol at reflux), and the work up complex (the crude product has to be kept in cool solvent and inert atmosphere). The subsequent N-benzylation, wherein acyl chloride was reacted with the trilactone trihydrochloride salt in the presence of triethylamine, afforded hexabenzylenenterobactin in moderate yields (79%),³⁴ but it was limited by the low solubility of the starting material in the cold tetrahydrofuran/methylene chloride mixture.

A facile one-pot reaction was developed to circumvent these problems. A slight excess of 2,3-bis(benzyloxy)benzoyl chloride (3.5 equiv) and tris(N-trityl-L-serine) trilactone were dissolved in chloroform and stirred at reflux for 7 h, to afford hexabenzylenenterobactin in decent yield (49%). The reaction mechanism is unknown. We postulate that trace water in solution initiates the hydrolysis of acyl chloride. HCl is formed as a byproduct, which then removes the N-trityl protecting group. This allows the
amine to attack the remaining acyl chlorides, regenerating HCl and ultimately forming hexabenzylenterobactin. Debenzylation via catalytic hydrogenation using Pd on carbon gives enterobactin in excellent yield (93%).

The coupling constants of the protons on the trilactone backbone give a lot of insight into the 3-dimensional structure of the compound. Tris(N-trityl-L-serine) trilactone has one large coupling constant, 11 Hz, and one small coupling constant, 4 Hz, to H₈ (Figure 21). This indicates that H₈ is anti to one of the vicinal hydrogens and gauche to the other, suggesting that the N-trityl group is equatorial. Tris(N-toluoyl-L-serine) trilactone displays two similar coupling constants to H₈, ~3.5 Hz. This indicates that H₈ is gauche to both vicinal hydrogens, showing a rearrangement of the N-toluoyl group to an axial orientation. o-Toluoyl is closer in size to 2,3-dihydroxybenzoyl so it is expected that enterobactin would have similar coupling constants. Instead, there is one small coupling, 4.5 Hz, and one medium coupling, 7.5 Hz, to H₈. There seems to be an equilibrium between the two conformations, wherein the side chains are directed either in an equatorial or an axial orientation, causing an averaging of the coupling constants.⁴⁰

![Figure 21](image_url)

**Figure 21.** The bulky trityl group encourages an equatorial orientation while the smaller o-toluoyl group allows for an axial orientation.

**Reactivity of Enterobactin with MoO₂(acac)₂.** In situ NMR studies were conducted between enterobactin and MoO₂(acac)₂. The insolubility of enterobactin in deuterated chloroform significantly slowed the delivery of the ligand to the Mo center.
Within 15 min of the reaction, the $^1$H NMR spectra revealed a set of new peaks, among which a singlet 4.28 (singlet) and two doublets at 4.51 and 4.83 are most notable. The three peaks have equal intensities and may correspond to the hydrogens in the trilactone backbone of the ligand. The product seems to have retained the $C_3$ symmetry of enterobactin. This geometry is consistent with the predicted tris(ligand) coordination to Mo similar to calculated Fe-enterobactin structures. However, after 24 h, the product peaks have disappeared. Unreacted MoO$_2$(acac)$_2$ still remains. One explanation is that the enterobactin-Mo(VI) complex has limited solubility in chloroform, and, upon accumulation, it precipitates from solution. To circumvent this problem, the reaction was conducted in more polar solvents, such as deuterated acetone and pyridine, which readily dissolve enterobactin. In both cases, multiple new peaks were observed, with no single major product. These peaks may correspond to dimers and oligomers of the enterobactin-molybdenum complex. It makes sense for aggregation to occur in acetone and pyridine, where there are equal amounts of Mo and enterobactin in solution, and not in chloroform, where there is a lower concentration of enterobactin.

### 3.4 Future Directions

**Addressing Issues of Aggregation.** One way of preventing oligomerization is to conduct the reaction with dilute concentrations of enterobactin. This approach may not be synthetically practical but it can at least help us determine the presence of the enterobactin-Mo(VI) complex via NMR and mass spectrometry. If the culprit does turn out to be aggregation, derivatives of the 2,3-dihydroxybenzamide side chain may be synthesized to circumvent this problem. Only catecholates with ortho hydrogens are
known to bridge two metal centers (Figure 22). Therefore, we will investigate a new ligand design wherein the position para to the amide carbon is occupied, effectively preventing aggregation through the catecholate oxygen.

Figure 22. Thermal ellipsoid plot of Tris(di-tert-butylcatechol)molybdenum(VI) dimer. Bridging of Mo centers via the oxygen ortho to H. Figure from Ref. 7b, reprinted by permission of the American Chemical Society.

Naphthoquinones provide the most promising targets since they are chemically more stable than ortho-benzoquinones. Hence, even if the oxidized form of the side chain dissociates from the metal center, it will remain intact and may reattach later on. Below is a target compound, a naphthoquinone ethyl ester (Figure 23).\(^4^1\) Diethyl succinate and 2,5-dimethoxybenzaldehyde undergo a Stobbe condensation to form a naphthalene ester. The acetyl protecting group is removed so that the phenol can be converted into a quinone using Co(salen).\(^4^1\)
Figure 23. Proposed reaction scheme for a new Naphthoquinone Ethyl Ester target.\textsuperscript{41}
A.1 Optical Spectroscopy

![UV-Visible Spectrum for Pb(DOPO\(^9\))\(_2\)](image1)

![UV-Visible Spectrum for Cr(DOPO\(^9\))(DOPO\(^{15}\))](image2)
A.2 Electrochemistry of Cr(DOPO)$_2$

A 1 mM dichloromethane solution of Cr(DOPO)$_2$ (9.25 mg in 10 mL) was prepared, using 0.1 M Bu$_4$NPF$_6$ as electrolyte. Electrochemical measurements were conducted in the drybox using a BAS Epsilon potentiostat. A standard three-electrode setup was used, with two glassy carbon electrodes serving as the working and counter electrodes, and a silver/silver chloride pseudo reference electrode. Potentials were referenced to ferrocene/ferrocenium at 0 V, with the reference potential measured by spiking the sample with a small amount of ferrocene. Cyclic voltammograms were recorded with a scan rate of 120 mV/sec.
### A.3 X-ray Crystallography

A.3.1 Selected Bond Lengths in Å

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</tr>
<tr>
<td>------------------</td>
<td>-------------</td>
<td>----------------------</td>
<td></td>
</tr>
<tr>
<td>M-O1</td>
<td>2.0448(14)</td>
<td>2.2470(33)</td>
<td></td>
</tr>
<tr>
<td>M-O2</td>
<td>2.0566(14)</td>
<td>2.3329(32)</td>
<td></td>
</tr>
<tr>
<td>M-O3</td>
<td>1.9914(14)</td>
<td>2.2468(33)</td>
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<tr>
<td>M-O4</td>
<td>1.9907(14)</td>
<td>2.3122(32)</td>
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</tr>
<tr>
<td>M-N1</td>
<td>1.9798(16)</td>
<td>2.3568(39)</td>
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<tr>
<td>M-N2</td>
<td>1.8767(16)</td>
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<tr>
<td>N1-C11</td>
<td>1.324(2)</td>
<td>1.3330(58)</td>
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</tr>
<tr>
<td>O1-C12</td>
<td>1.303(2)</td>
<td>1.2977(55)</td>
<td></td>
</tr>
<tr>
<td>C11-C12</td>
<td>1.429(3)</td>
<td>1.4208(65)</td>
<td></td>
</tr>
<tr>
<td>C12-C13</td>
<td>1.418(3)</td>
<td>1.4161(67)</td>
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</tr>
<tr>
<td>C13-C14</td>
<td>1.390(3)</td>
<td>1.3806(66)</td>
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</tr>
<tr>
<td>C14-C15</td>
<td>1.438(3)</td>
<td>1.4213(66)</td>
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</tr>
<tr>
<td>C15-C16</td>
<td>1.377(3)</td>
<td>1.3761(66)</td>
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<tr>
<td>C11-C16</td>
<td>1.411(3)</td>
<td>1.4076(65)</td>
<td></td>
</tr>
<tr>
<td>N1-C21</td>
<td>1.318(2)</td>
<td>1.3161(57)</td>
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<tr>
<td>O2-C22</td>
<td>1.289(2)</td>
<td>1.2731(54)</td>
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<td>C21-C22</td>
<td>1.438(3)</td>
<td>1.4491(67)</td>
<td></td>
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<tr>
<td>C22-C23</td>
<td>1.423(3)</td>
<td>1.4276(66)</td>
<td></td>
</tr>
<tr>
<td>C23-C24</td>
<td>1.376(3)</td>
<td>1.3740(65)</td>
<td></td>
</tr>
<tr>
<td>C24-C25</td>
<td>1.443(3)</td>
<td>1.4411(66)</td>
<td></td>
</tr>
<tr>
<td>C25-C26</td>
<td>1.367(3)</td>
<td>1.3598(64)</td>
<td></td>
</tr>
<tr>
<td>C21-C26</td>
<td>1.422(3)</td>
<td>1.4240(66)</td>
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</tr>
<tr>
<td>N2-C31</td>
<td>1.348(2)</td>
<td></td>
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</tr>
<tr>
<td>O3-C32</td>
<td>1.333(2)</td>
<td>Mo-O11</td>
<td></td>
</tr>
<tr>
<td>C31-C32</td>
<td>1.405(3)</td>
<td>Mo-O12</td>
<td></td>
</tr>
<tr>
<td>C32-C33</td>
<td>1.407(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C33-C34</td>
<td>1.400(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C34-C35</td>
<td>1.407(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C35-C36</td>
<td>1.386(3)</td>
<td></td>
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</tr>
<tr>
<td>C31-C36</td>
<td>1.399(3)</td>
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</tr>
<tr>
<td>N2-C41</td>
<td>1.350(3)</td>
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</tr>
<tr>
<td>O4-C42</td>
<td>1.337(2)</td>
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</tr>
<tr>
<td>C41-C42</td>
<td>1.409(3)</td>
<td></td>
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<tr>
<td>C42-C43</td>
<td>1.397(3)</td>
<td></td>
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<tr>
<td>C43-C44</td>
<td>1.406(3)</td>
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<tr>
<td>C44-C45</td>
<td>1.412(3)</td>
<td></td>
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<tr>
<td>C45-C46</td>
<td>1.384(3)</td>
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<tr>
<td>C41C46</td>
<td>1.398(3)</td>
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</table>
A.3.2 Selected Bond Angles in degrees (°)

<table>
<thead>
<tr>
<th></th>
<th>Pb(DOPO$^Q$)$_2$</th>
<th>Cr(DOPO)$_2$</th>
<th>W(DOPO$^{Cat}$)$_2$</th>
<th>Mo(DOPO$^{Cat}$)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1-M-N1</td>
<td>65.65(8)</td>
<td>77.38(6)</td>
<td>74.90(7)</td>
<td>75.12(10)</td>
</tr>
<tr>
<td>O1-M-O2</td>
<td>123.64(7)</td>
<td>154.16(5)</td>
<td>149.47(6)</td>
<td>150.20(8)</td>
</tr>
<tr>
<td>O1-M-N2</td>
<td>70.01(8)</td>
<td>105.39(6)</td>
<td>106.81(7)</td>
<td>107.06(9)</td>
</tr>
<tr>
<td>O1-M-O4</td>
<td>80.52(7)</td>
<td>91.85(6)</td>
<td>91.83(7)</td>
<td>91.74(9)</td>
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<tr>
<td>N1-M-O2</td>
<td>59.40(7)</td>
<td>76.79(6)</td>
<td>74.57(7)</td>
<td>75.09(10)</td>
</tr>
<tr>
<td>N1-M-O4</td>
<td>143.06(8)</td>
<td>100.28(6)</td>
<td>103.67(7)</td>
<td>103.38(9)</td>
</tr>
<tr>
<td>N2-M-N1</td>
<td>117.01(8)</td>
<td>177.15(7)</td>
<td>177.56(8)</td>
<td>177.11(10)</td>
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<tr>
<td>N2-M-O2</td>
<td>148.15(8)</td>
<td>100.45(6)</td>
<td>103.69(7)</td>
<td>102.71(9)</td>
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<td>N2-M-O4</td>
<td>59.76(7)</td>
<td>79.05(6)</td>
<td>74.66(7)</td>
<td>74.81(9)</td>
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<td>O3-M-O1</td>
<td>88.79(8)</td>
<td>95.86(6)</td>
<td>97.90(7)</td>
<td>98.16(9)</td>
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<tr>
<td>O3-M-N1</td>
<td>70.39(8)</td>
<td>101.63(6)</td>
<td>106.91(7)</td>
<td>106.55(9)</td>
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<tr>
<td>O3-M-O2</td>
<td>84.41(8)</td>
<td>89.45(6)</td>
<td>91.42(7)</td>
<td>90.78(9)</td>
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<tr>
<td>O3-M-N2</td>
<td>66.21(8)</td>
<td>78.91(6)</td>
<td>74.71(7)</td>
<td>75.19(9)</td>
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<tr>
<td>O3-M-O4</td>
<td>125.39(7)</td>
<td>157.87(6)</td>
<td>149.35(6)</td>
<td>1.49.98(8)</td>
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<tr>
<td>O4-M-O2</td>
<td>144.26(7)</td>
<td>92.59(6)</td>
<td>94.77(7)</td>
<td>94.55(8)</td>
</tr>
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MoO$_2$(DOPO$^Q$)$_2$

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>O1-M-N1</th>
<th>O1-M-O2</th>
</tr>
</thead>
<tbody>
<tr>
<td>O12-M-O11</td>
<td>104.50(16)</td>
<td>66.94(14)</td>
<td>133.09(12)</td>
</tr>
<tr>
<td>O12-M-O3</td>
<td>145.80(14)</td>
<td>133.09(12)</td>
<td>65.14(13)</td>
</tr>
<tr>
<td>O12-M-O1</td>
<td>94.24(14)</td>
<td>133.09(12)</td>
<td>70.55(12)</td>
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<tr>
<td>O12-M-O4</td>
<td>78.18(14)</td>
<td>133.09(12)</td>
<td>66.30(14)</td>
</tr>
<tr>
<td>O12-M-N2</td>
<td>143.67(16)</td>
<td>133.09(12)</td>
<td>66.30(14)</td>
</tr>
<tr>
<td>O12-M-O2</td>
<td>82.46(13)</td>
<td>133.09(12)</td>
<td>66.30(14)</td>
</tr>
<tr>
<td>O12-M-N1</td>
<td>81.35(15)</td>
<td>133.09(12)</td>
<td>66.30(14)</td>
</tr>
<tr>
<td>O11-M-O3</td>
<td>91.08(14)</td>
<td>133.09(12)</td>
<td>66.30(14)</td>
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<tr>
<td>O11-M-O1</td>
<td>144.78(13)</td>
<td>133.09(12)</td>
<td>66.30(14)</td>
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<td>O11-M-O4</td>
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</tr>
<tr>
<td>O11-M-N2</td>
<td>82.75(14)</td>
<td>133.09(12)</td>
<td>66.30(14)</td>
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<tr>
<td>O11-M-O2</td>
<td>79.59(13)</td>
<td>133.09(12)</td>
<td>66.30(14)</td>
</tr>
<tr>
<td>O11-M-N1</td>
<td>144.48(16)</td>
<td>133.09(12)</td>
<td>66.30(14)</td>
</tr>
<tr>
<td>O4-M-O2</td>
<td>150.75(0.11)</td>
<td>133.09(12)</td>
<td>66.30(14)</td>
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### A.3.3 Crystal Data

<table>
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<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{68}H_{88}N_{2}O_{6}Pb</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1236.59</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>120.2</td>
</tr>
<tr>
<td>Crystal system</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pbca</td>
</tr>
<tr>
<td>a, Å</td>
<td>18.2299(17)</td>
</tr>
<tr>
<td>b, Å</td>
<td>16.8979(16)</td>
</tr>
<tr>
<td>c, Å</td>
<td>39.677(4)</td>
</tr>
<tr>
<td>α, deg</td>
<td>90</td>
</tr>
<tr>
<td>β, deg</td>
<td>90</td>
</tr>
<tr>
<td>γ, deg</td>
<td>90</td>
</tr>
<tr>
<td>Volume, Å³</td>
<td>12222(2)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>ρ_{calc}, mg/mm³</td>
<td>1.344</td>
</tr>
<tr>
<td>μ, mm⁻¹</td>
<td>2.813</td>
</tr>
<tr>
<td>F(000)</td>
<td>5120.0</td>
</tr>
<tr>
<td>Crystal size, mm³</td>
<td>0.24 × 0.19 × 0.06</td>
</tr>
<tr>
<td>2Θ range for data collection</td>
<td>3.04 to 56.82°</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>205665</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>15345 [R(int) = 0.0578]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>15345/0/694</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.083</td>
</tr>
<tr>
<td>Final R indexes [I&gt;=2σ (I)]</td>
<td>R₁ = 0.0371, wR₂ = 0.0834</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.0544, wR₂ = 0.0897</td>
</tr>
</tbody>
</table>
Empirical formula \( \text{C}_{56}\text{H}_{76}\text{N}_{2}\text{O}_{6}\text{Cr} \)

Formula weight 925.19

Temperature, K 120.0

Crystal system monoclinic

Space group \( C2/c \)

\( a, \text{Å} \) 40.261(4)

\( b, \text{Å} \) 12.7201(11)

\( c, \text{Å} \) 25.355(3)

\( \alpha, \text{deg} \) 90

\( \beta, \text{deg} \) 124.543(4)

\( \gamma, \text{deg} \) 90

Volume, \( \text{Å}^3 \) 10695.7(19)

\( Z \) 8

\( \rho_{\text{calc}}, \text{mg/mm}^3 \) 1.149

\( \mu, \text{mm}^{-1} \) 0.262

\( F(000) \) 3984.0

Crystal size, mm\(^3\) 0.25 \( \times \) 0.19 \( \times \) 0.13

2\( \Theta \) range for data collection 2.46 to 52.84°

Reflections collected 78777

Independent reflections 10975 [R(int) = 0.0496]

Data/restraints/parameters 10975/0/610

Goodness-of-fit on \( F^2 \) 1.057

Final R indexes \([I \geq 2\sigma(I)]\) \( R1 = 0.0444, wR2 = 0.1135 \)

Final R indexes [all data] \( R1 = 0.0661, wR2 = 0.1290 \)
Empirical formula \( \text{C}_{56}\text{H}_{76}\text{N}_2\text{O}_6\text{W} \)

Formula weight 1057.03

Temperature, K 120.0

Crystal system monoclinic

Space group \( P2_1/c \)

\( a, \text{ Å} \)
20.5540(12)

\( b, \text{ Å} \)
19.8902(12)

\( c, \text{ Å} \)
12.9611(8)

\( \alpha, \text{ deg} \)
90

\( \beta, \text{ deg} \)
91.0740(10)

\( \gamma, \text{ deg} \)
90

Volume, \( \text{Å}^3 \)
5297.9(6)

\( Z \)
4

\( \rho \text{calc}, \text{ mg/mm}^3 \)
1.325

\( \mu, \text{ mm}^{-1} \)
2.229

\( F(000) \)
2192

Crystal size, \( \text{mm}^3 \)
0.19 \( \times \) 0.15 \( \times \) 0.14

2\( \Theta \) range for data collection 1.98 to 56.77°

Reflections collected 71487

Independent reflections 13261 [R(int) = 0.0354]

Data/restraints/parameters 13261/0/610

Goodness-of-fit on \( F^2 \) 1.045

Final R indexes [I>2\( \sigma \)(I)] \( R_1 = 0.0230, wR_2 = 0.0529 \)

Final R indexes [all data] \( R_1 = 0.0318, wR_2 = 0.0571 \)
Empirical formula \( \text{C}_{56}\text{H}_{76}\text{N}_{2}\text{O}_{6}\text{Mo} \)

Formula weight 969.15

Temperature, K 120.0

Crystal system monoclinic

Space group \( P2_1/c \)

\( a, \text{Å} \) 20.5177 (23)

\( b, \text{Å} \) 19.8599(22)

\( c, \text{Å} \) 12.9284(14)

\( \alpha, \text{deg} \) 90

\( \beta, \text{deg} \) 91.849(2)

\( \gamma, \text{deg} \) 90

Volume, \( \text{Å}^3 \) 5267.48(1.71)

\( Z \) 4

\( \rho\text{calc}, \text{mg/mm}^3 \) 1.222

\( \mu, \text{mm}^{-1} \) 0.30

\( F(000) \) 2064

Crystal size, \( \text{mm}^3 \) 0.227 \( \times \) 0.121 \( \times \) 0.044

2\( \Theta \) range for data collection 1.98 to 53.05°

Reflections collected 39476

Independent reflections 10869 [R(int) = 0.1257]

Data/restraints/parameters 10869/0/610

Goodness-of-fit on \( F^2 \) 0.927

Final R indexes \([I>=2\sigma (I)]\) R1 = 0.0503, wR2 = 0.0980

Final R indexes [all data] R1 = 0.1153, wR2 = 0.0927
Empirical formula \( \text{C}_{56}\text{H}_{76}\text{N}_{2}\text{O}_{10}\text{Mo} \)

Formula weight 1001.13

Temperature, K 120.0

Crystal system monoclinic

Space group \( P2_1/n \)

\( a, \text{Å} \) 20.2266(16)

\( b, \text{Å} \) 27.459(2)

\( c, \text{Å} \) 20.4708(16)

\( \alpha, \text{deg} \) 90

\( \beta, \text{deg} \) 110.0796(19)

\( \gamma, \text{deg} \) 90

Volume, \( \text{Å}^3 \) 10678.6(15)

\( Z \) 8

\( \rho_{\text{calc}}, \text{mg/mm}^3 \) 1.245

\( \mu, \text{mm}^{-1} \) 0.299

\( F(000) \) 4256

Crystal size, \( \text{mm}^3 \) 0.11 \( \times \) 0.09 \( \times \) 0.07

2\( \Theta \) range for data collection 2.96 to 41.86°

Reflections collected 131390

Independent reflections 11361 [R(int) = 0.1942]

Data/restraints/parameters 11361/6/1255

Goodness-of-fit on \( F^2 \) 0.987

Final R indexes [I>=2\( \sigma \) (I)] \( R1 = 0.0468 \), w\( R2 = 0.0877 \)

Final R indexes [all data] \( R1 = 0.0909 \), w\( R2 = 0.0991 \)


28) Brown, S.N. Unpublished Results.


