UNIVERSITY OF ILLINOIS CHICAGO

Honors College

Synthesis and Characterization of Redox-active Dimolybdenum Complexes for Nonaqueous Redox Flow Batteries

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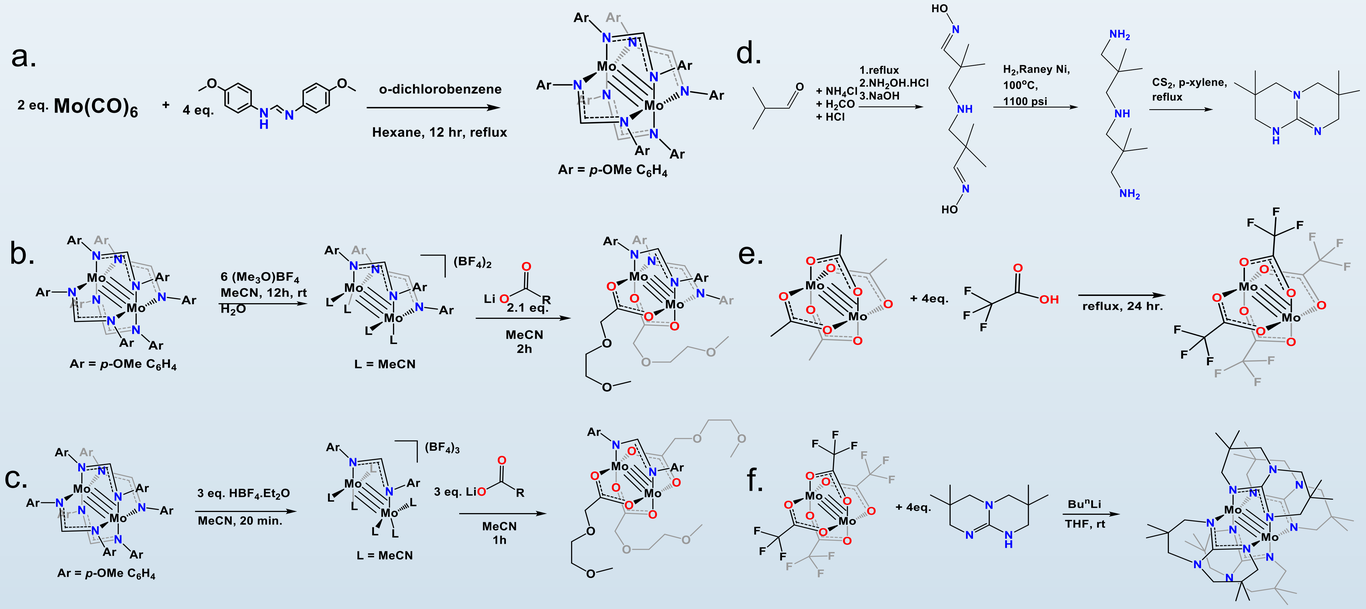
Abstract

In this project, mixed ligand bimetallic complexes of diaryl formamidinate (**DAniF** - N,N′-di-p-anisylformamidinate), cyclic guanidinate (**TMhpp** - 3,3,9,9-tetramethyl-1,5,7triazabicyclo[4.4.0]dec-4-ene), and acetate ether ligands (**AE** - 2-(2-methoxyethoxy)acetate) were synthesized to investigate and tune the electrochemical and solubility properties. Solubility measurements showed the $Mo_2(DAniF)(AE)_3$ complex (3:1) to have solubility of 65.8 ±2.6 mM in acetonitrile and the cis-$Mo_2(DAniF)_2(AE)_2$ complex (cis) to have solubility of 201.3 ± 5.3 mM in acetonitrile. CV data was obtained for both cis and 3:1 complexes in acetonitrile. Single electronic events occur at -0.33 V *vs.* Fc/Fc$^+$ for cis and -0.18 V *vs.* Fc/Fc$^+$ for 3:1. $Mo_2(TMhpp)_4$ was found to have two electronic events which occur at -0.5 V and -1.4 V vs. Fc/Fc+ which correspond to the $Mo_2^{5+/4+}$ and $Mo_2^{6+/5+}$ processes respectively.

Background

Energy consumption has dramatically increased globally, leading to different avenues for energy storage systems with the goal of decreasing dependence on fossil fuels.[1,2] Many industrial systems use redox-flow cells to support grid scale energy storage. This study utilizes dimolybdenum complexes which contain a δ bond. The δ-δ* orbitals are both higher in energy as well as redox-active. Quadruply-bonded bimetallic complexes are well known for their unique electronic properties and use as strong reducing agents.[3] With this aim, dimolybdenum complexes have been shown to serve in potential energy storage systems for redox-flow batteries.[4] The solvent of interest is acetonitrile due to the potential window of 5V. In this project, bicyclic guanidinate ligands were also synthesized with methyl groups with the aim of increasing redox potential ranges as well as enhancing solubility character.[5]

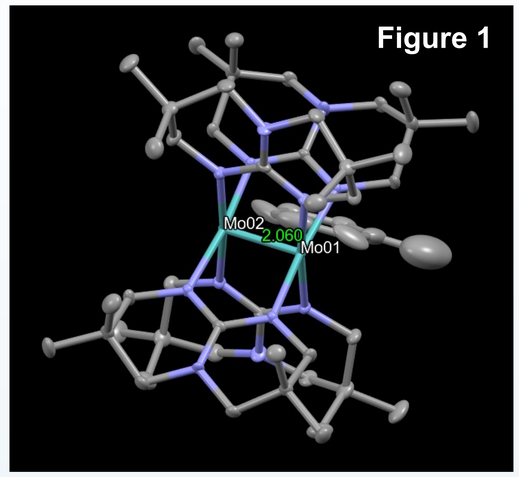
Synthetic Schemes

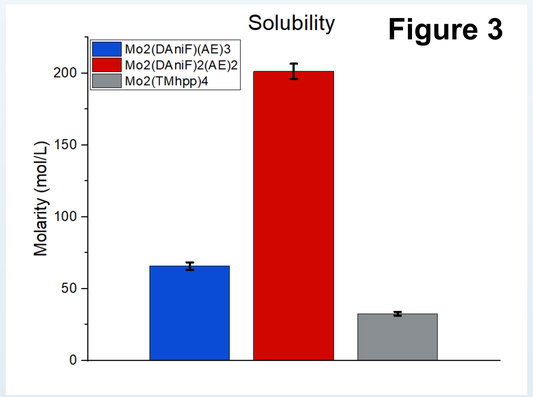


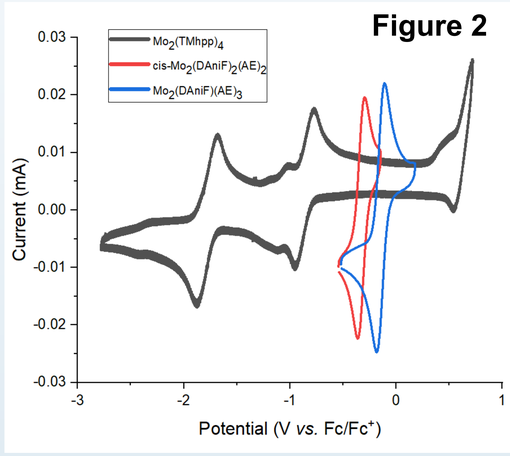
Schemes a,b,c,e,f were adopted from the inorganic literature. Scheme d adopted from patent literature for ligand synthesis. Compounds were characterized with ^{1}H NMR, ^{13}C NMR, and IR.

Results and Discussion

- **(Figure 1)** Crystalized $Mo_2(TMhpp)_4$ compound with vapor diffusion and obtained single crystal XRD structure.
- **(Figure 2)** The oxidation potential for cis and 3:1 complexes occur at mild negative potentials. $Mo_2(TMhpp)_4$ complex shows two electron oxidations at more negative potentials.
- **(Figure 3)** Trend for solubility shows cis as having greatest solubility in acetonitrile.
- **Future studies** with mixed DAniF, AE. and TMhpp Mo_2 complexes to increase solubility in acetonitrile.
- Electrochemical analyses with mixed TMhpp complexes.







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References

(1) Hoffert,M.I; Caldeira, k.; Jain, A. K.; Haites, E.F.; Harvey, L. D.; Potter, S.D.; Schlesinger, M.E.; Schneider, S.H.; Watts, R. G.; Wigley, T. M. I.; Wuebbles, D. J. Nature. 1998, 395, 881
(2) Sánchez-Díez, E.; Ventosa, E.; Guarnieri, M.; Trovò, A.; Flox, C.; Marcilla, R.; Soavi, F.; Mazur, P.; Aranzabe, E.; Ferret, R. Redox Flow Batteries: Status and Perspective towards Sustainable Stationary Energy Storage. Journal of Power Sources 2021, 481, 228804. https://doi.org/10.1016/j.jpowsour.2020.228804.
(3) Cotton, F. A.; Murillo, C. A.; Wang, X.; Wilkinson, C. C. Increasing the Solubility of Strong Reducing Agents Containing Mo24+ Units and Alkyl-Substituted Guanidinate Ligands. Dalton Trans. 2007, No. 35, 3943. https://doi.org/10.1039/b707201e.
(4) Rodríguez-López, N.; Metta, N.; Metta-Magana, A. J.; Villagrán, D. Redox Potential Tuning of Dimolybdenum Systems through Systematic Substitution by Guanidinate Ligands. Inorg. Chem. 2020, 59 (5), 3091–3101. https://doi.org/10.1021/acs.inorgchem.9b03394.
(5) Coles, M. P. Bicyclic-Guanidines, -Guanidinates and -Guanidinium Salts: Wide Ranging Applications from a Simple Family of Molecules. Chem. Commun. 2009, No. 25, 3659. https://doi.org/10.1039/b901940e.