

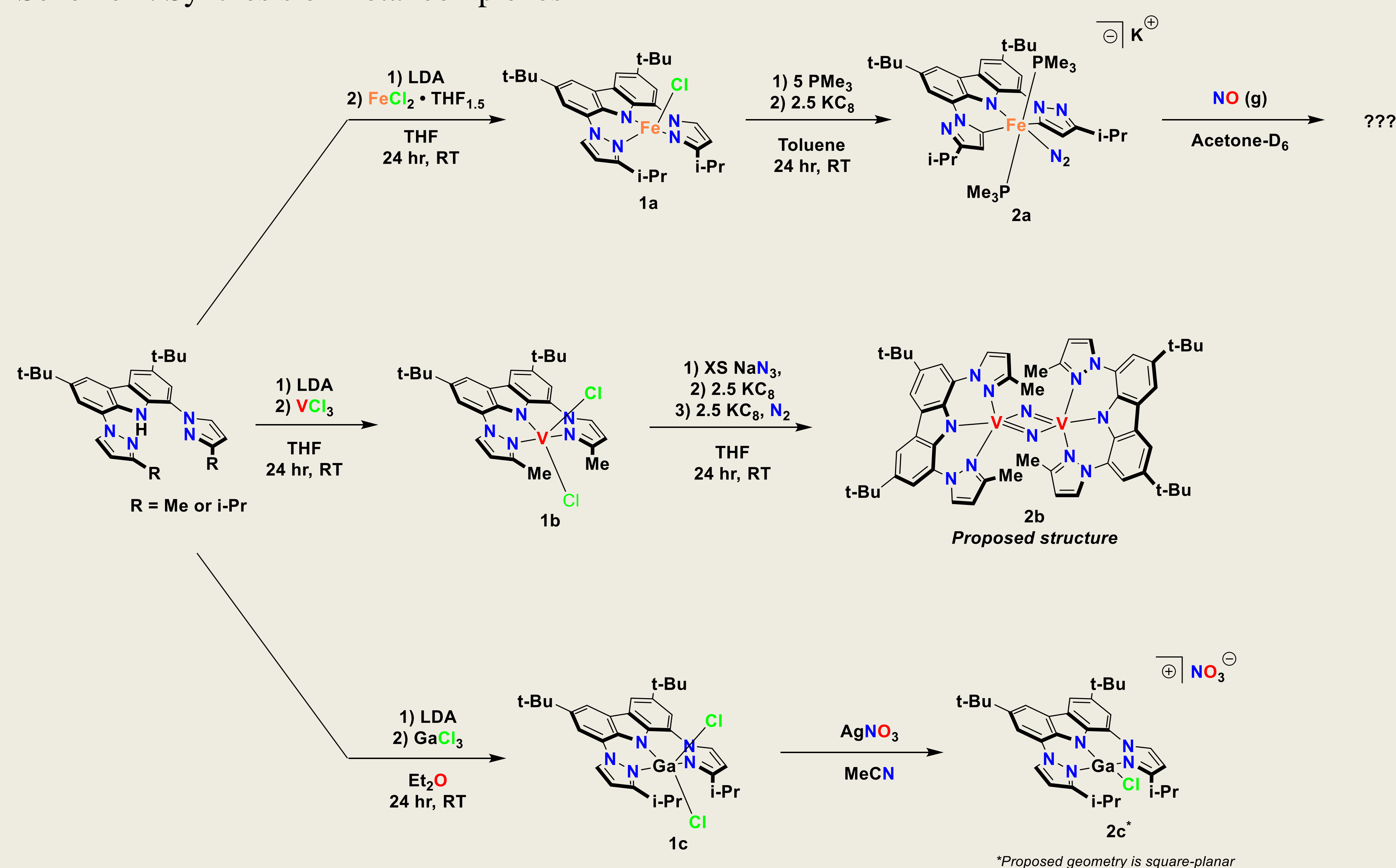
Investigation and Characterization of a Series of Novel NNN-Pincer Ligand Complexes with Iron, Vanadium, and Gallium Metal Centers

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Introduction

Tridentate-chelating ligands with coplanar donors in adjacent positions, known as pincer ligands, have long been studied in their support of a wide array of transition and main group metals.¹ Among the many types of pincer ligands, NNN-pincer based ligand systems and their derivatives are attractive targets in coordination and organometallic chemistry. NNN-pincer chemistry benefits from facile modification of the ligand backbone, reduced tendency to be oxidized under aerobic conditions compared to P-donor type of ligands, and support of metal centers of varying size and charge. These factors combine to furnish a variety of oxidation states of metals. Additionally, recent literature suggests that gallium complexes may be used as anti-cancer agents, and nitrogen-bound iron and vanadium complexes can serve as catalysts for organic reactions and nitrogen activation.^{2,3,4,5} Our research builds off these findings and looks to investigate the wide array of effects that a series of novel, monoanionic NNN-pincer ligand may have, once complexed with various metal centers such as iron, vanadium, and gallium.

Scheme 1. Synthesis of metal complexes



Methodology

Due to the oxygen and moisture sensitivity of these complexes, all manipulations were performed under a nitrogen atmosphere using standard Schlenk Line techniques or in an M. Braun UNILab Pro glovebox. The syntheses of each complex are as shown (Scheme 1). All glassware was dried at 150 °C overnight. Diethyl ether, tetrahydrofuran, and toluene were purified using a Pure Process Technology solvent purification system. ¹H NMR data were recorded on Varian Inova 300 or 500 MHz spectrometer at 22 °C. Fourier transform-infrared (FTIR) spectroscopy was performed using a Thermo Scientific Nicolet Nexus 470 FT-IR E.S.P., FTIR spectrometer. Elemental analysis was conducted by Midwest Microlab, LLC. (Indianapolis, IN). Crystals were grown through common means such as slow-diffusion of *n*-pentane into a THF solution at either ambient temperatures or -20 °C. Suitable crystals were analyzed using X-Ray diffraction by Dr. Matthias Zeller at Purdue University (West Lafayette, IN). Structures, in CIF format, are as shown (Figures 1-3).

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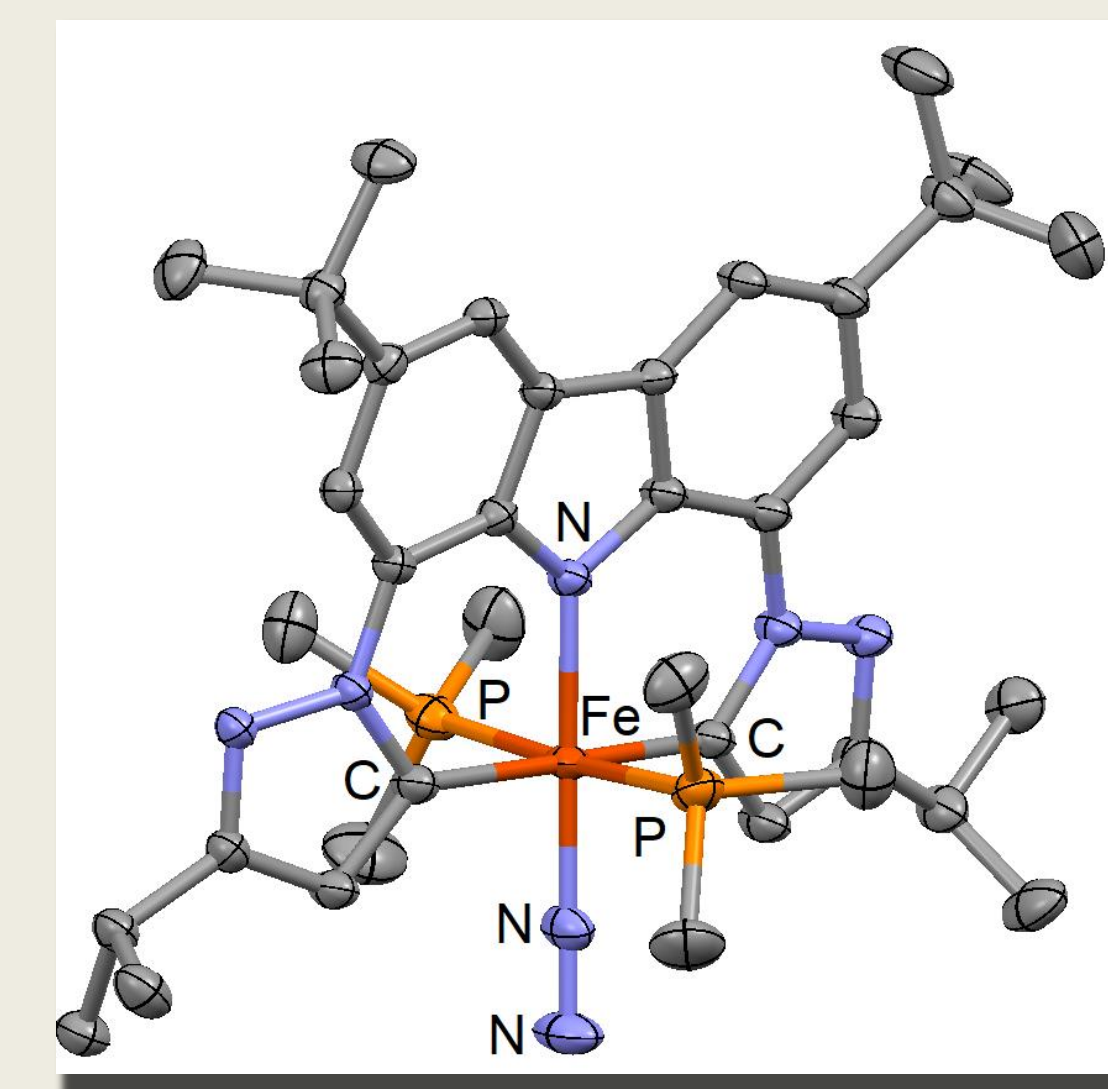


Figure 1. Molecular structure of 2a with thermal ellipsoids at the 50% probability level. Hydrogen atoms and counterions omitted for clarity. (grey = C, blue = N, red = Fe, orange = P).

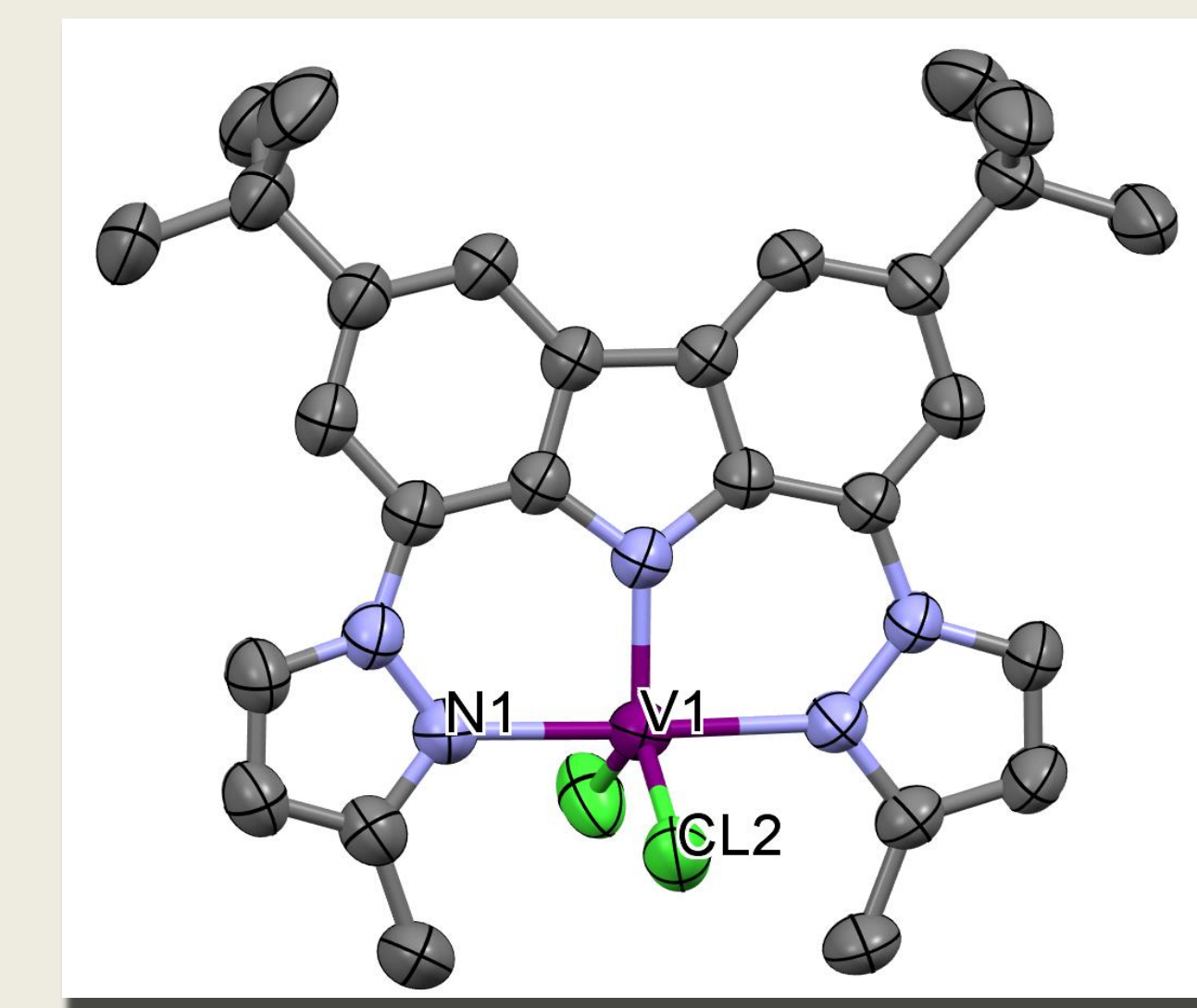


Figure 2. Molecular Structure of 1b with thermal ellipsoids at the 50% probability level. Hydrogen atoms omitted for clarity. (grey = C, blue = N, purple = V, green = Cl).

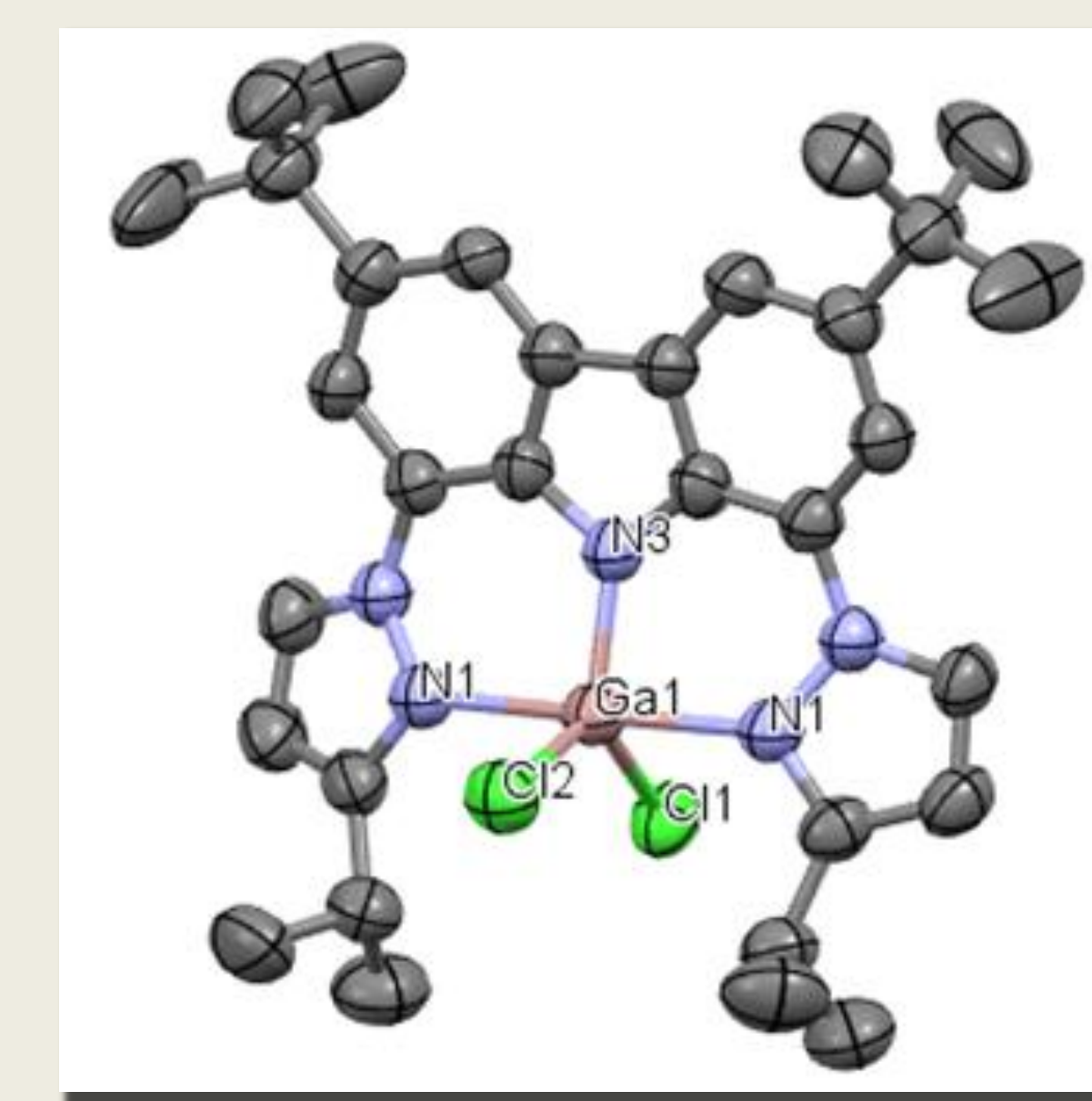


Figure 3. Molecular Structure of 1c with thermal ellipsoids at the 80% probability level. Hydrogen atoms omitted for clarity. (grey = C, blue = nitrogen, pink = Ga, green = Cl).

Conclusion

Though this research is still ongoing, our findings show high promise for use of the reported iron, vanadium, and gallium complexes as catalysts and anti-cancer agents. To date, much success has been had in the synthesis and characterization of these complexes through ¹H NMR spectroscopy, X-ray crystallography, mass spectrometry. Future work will include testing the catalytic extents of these complexes in numerous organic reactions such as cycloaddition, polymerization, and epoxide coupling. Additional tests may be done to characterize the anti-cancer potential of the synthesized Gallium complexes.

Citations

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