Synthesizing molecular magnets

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Abstract

Single-molecule magnets, or SMMs, arise when certain molecule species retain a magnetic moment after an applied magnetic field is removed. By changing the coordination around the central metal atom, different magnetic and structural properties are observed. The primary objective of the research program is to synthesize new mononuclear transition metal compounds that are SMMs. Previous research results from the Richeson group have shown that coordination compounds of cobalt (II) with planar tridentate ligands yield new SMMs. To study these compounds, organic syntheses to obtain the ligands were performed. These ligands were then reacted with a metal compound, and the physical features of the SMM were analyzed through studying crystal structure and NMR. These geometric variations will be tabulated in order to find metal coordination geometries that lead to significant spin-orbit coupling. These results will shed light on the role of spin-orbit coupling in slow relaxation of the magnetization.

Introduction

Properties of magnets are well described by the laws of physics on macroscopic and microscopic levels. However, at the molecular level, these properties can be manipulated based on the structure of the molecule. By binding cobalt, a paramagnetic species, to different forms of a bis(imino)pyridine ligand, it is believed that the magnetic properties of the cobalt compound can be altered.

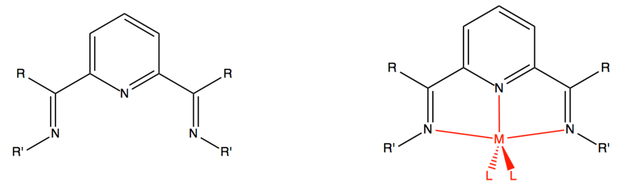


Figure 1: Structure of the general bis(imino)pyridine ligand (left) and the ligand bound to an example metal compound ML_2 (right)

What is already known?

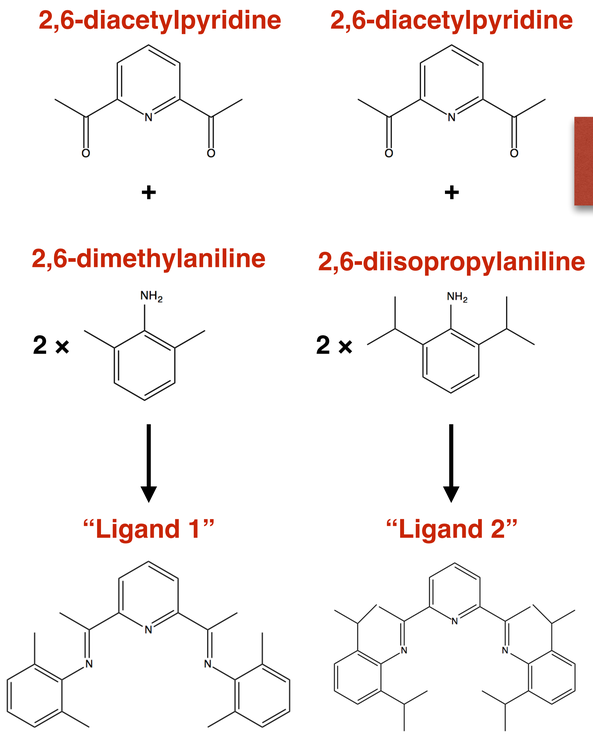
- The tridentate ligands synthesized in this project were known to be planar molecules.
- Cobalt and cobalt compounds are well known to have magnetic properties.
- Coordination compounds of cobalt synthesized with planar tridentate ligands have been synthesized in the past, and have yielded SMMs.
- Tridentate ligands are easily synthesized by organic synthesis, and existing procedures exist to create them.

What is not already known?

- Not all cobalt coordination compounds with tridentate ligands have been synthesized – their properties are unknown and unreported. This project will aim to create brand new products.

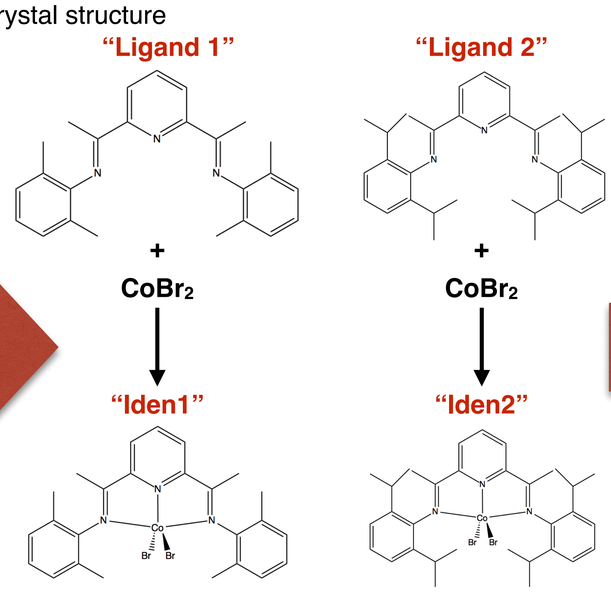
1 - Synthesis of ligands

- Through a series of organic syntheses, the tridentate ligands were created.
- The starting materials for the reaction involved 2,6-diacetylpyridine (the “diketone”) and an amine.
  - The creation of “Ligand 1” involved the use of 2,6-dimethylaniline as the amine, and 2,6-diisopropylaniline for “Ligand 2”.
- **Procedure:** The reactions were performed by the addition of the amine to the diketone. Formic acid was used as an initiator for the action to proceed. The reactions were done at 100°C in methanol, and generally took 24 hours to be completed.
- **Isolation of product:** The ligand products “Ligand 1” and “Ligand 2” were both insoluble in methanol, and isolation was easily performed via suction filtration.



2 - Synthesis of cobalt compounds

- The cobalt compounds were synthesized through organometallic synthesis
- The starting materials for the reaction involved a ligand and cobalt (II) bromide ($CoBr_2$)
  - The reaction of cobalt (II) bromide with “Ligand 1” yielded a compound given the name “Iden1”, and the reaction with “Ligand 2” yielded a compound named “Iden2”
- The reactions were synthesized by direct addition of the starting materials, and then recrystallized to determined the crystal structure



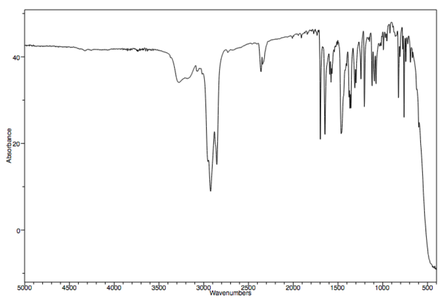


Figure 2: Example of IR Spectroscopy of “Ligand 1”. In the adjacent IR diagram, it can be seen that the peak at around 3000 cm^{-1} corresponds to the sp^3 hybridized C-H bonds, and that the peaks at around 1600 cm^{-1} correspond to the aromatic C-C bonds. IR spectroscopy helps in identifying molecular structure.

3 - Results

- Following the recrystallization of Iden1 and Iden2, the purity will be determined by analyzing the crystal structure of the cobalt coordination compounds
  - This will be done through x-ray crystallography.
- The magnetic properties of these compounds can be tested by measuring the magnetic moment of the compound after an external magnetic field is removed.
- The purity of the ligands was tested as part of this project, exploring spectroscopic techniques such as infrared spectroscopy (IR) and nuclear magnetic resonance (NMR).

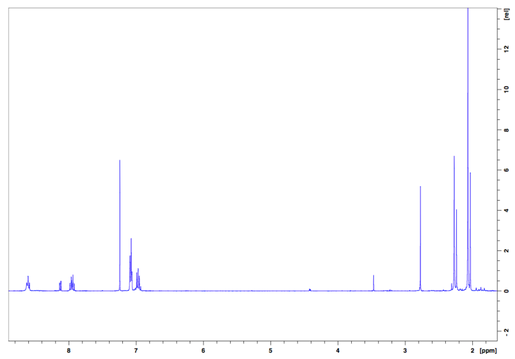


Figure 3: NMR data for “Ligand 1”

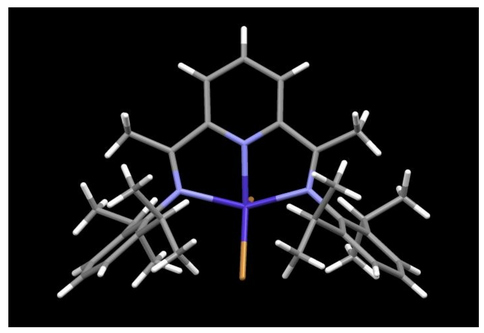


Figure 4: Crystal structure of “Iden2” using x-ray crystallography

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