An investigation of the potential spin-crossover properties of Co(phen)$_2$(NCS)$_2$

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Abstract: In this project, we synthesized a cobalt-containing complex and attempted to characterize its electronic structure using a variety of experimental and computational techniques. Our TGA+electromagnet findings yielded promising initial results about the compound's spin crossover properties, but the compound may have degraded, so further research is needed to confirm these properties. We plan to collaborate with other institutions that have SQUID magnetometers to further contribute to the growing body of research on spin crossover materials and their properties.

1 Introduction

Spin crossover is a property exhibited by certain transition metal complexes where the electronic properties of the material change in response to external stimuli, such as temperature, pressure, or light. The phenomenon is caused by the splitting of the d orbital of the metal, which allows for both high-spin and low-spin configurations. In the high-spin configuration, the complex adopts a configuration with more unpaired electrons because it is thermodynamically favorable for the electron to move up to the next orbital rather than couple with another electron in the lower orbital. In the low-spin configuration, the energy gap is large enough that this "jump" is not thermodynamically favorable.

In this project, I synthesized and attempted to characterize the electronic structure of Co(phen)$_2$(NCS)$_2$ in an attempt to further understand its possible spin crossover properties. This compound potentially exhibits spin crossover properties, since the Fe analog (Fe(phen)$_2$(NCS)$_2$) has been demonstrated to exhibit the desired property. To characterize the spin crossover properties of the cobalt compound, I attempted to use IR, Raman, and TGA techniques, where TGA proved most useful, and would ideally use SQUID magnetometry.

I also attempted to use DFT techniques to computationally predict the electronic structure of both the high- and low-spin forms of Co(phen)$_2$(NCS)$_2$. This was done in an attempt to be able to compare experimental and computational data to better understand the properties of the compound. By better understanding the properties of the spin crossover of this particular compound, we hope to further our understanding of the broader mechanism by which spin crossover happens.

Because spin-crossover often exhibits a hysteresis curve (the material can exist in either state given certain conditions depending on its past), these materials can have the ability to store information, leading to interesting applications for non-NAND memory devices. Also, since these compounds are able to respond to external stimulus, there is research into their applications as sensors of heat/light.

2 Materials & Methods

2.1 Synthesis

The synthesis of Co(phen)$_2$(NCS)$_2$ was carried out according to the procedure described by **?**. 0.4217 g of cobalt (II) sulfate hexahydrate were dissolved in approximately 50 mL of water. Then, 0.2933 g of KSCN were added to the solution, followed by approximately 25 mL of water to ensure that the thermometer was immersed in the solution. A solution of 0.5417 g of 1,10-phenanthroline in 50 mL of water was added dropwise to the reaction vessel, resulting in the formation of a hot pink precipitate. The precipitate was vacuum filtered after 5 minutes to ensure complete precipitation, and then washed with water and ethanol. The resulting compound was dried under vacuum overnight and had a final dry mass of 0.641 g, yielding 80%.

2.2 Characterization Methods

2.2.1 Melting Point

Melting point characterization was attempted on an SRS Digimelt MPA160.

2.2.2 IR

IR Spectra of the compound were taken on a Bruker Alpha in the solid state.

2.2.3 Raman

We used a Renishaw Raman microscope to take spectra of the compound, with a 785nm laser and 1200l/mm grating. The compound was placed onto a glass slide in the solid state. This slide was then placed in a temperature-controlled heating stage.

2.2.4 TGA

All TGA was carried out on a TA Instruments TGA5500. Initial decomposition experiments used an alumina ceramic pan, and all subsequent experiments used aluminum pans with stainless steel bales. All samples were put directly in the pans.

2.2.5 SQUID

Our initial contact for SQUID magnetometry had a temporarily non-functional instrument. SQUID has proven to be

one of the most powerful techniques for characterizing spin crossover compounds, and we are in touch with a number of other institutions in the area that may be able to help us accomplish SQUID magnetometry of our desired compound.

2.3 Computational Investigations

Computational studies were carried out on a HPC cluster at Colorado College. Initial calculations were performed using ORCA 4.2.1 and later calculations wtih ORCA 5.0.3. Initial pre-optimization XYZ coordinates were calculated using Avogadro on Mac OS X. The calculations used a B3LYP basis set. Full information on alternate basis sets, convergence criteria, etc. can be found in the supplemental information. We were able to successfully complete geometry optimization and attempted vibrational frequency calculation of Raman and IR spectra.

3 Results & Discussion

3.1 Experimental

This compound proved elusive to characterization techniques. Initial melting point measurements were unsuccessful, given that the instrument only goes up to 260 °C.

TGA proved to be the most useful technique we had accessible to us, and was the only confirmation of possible spin crossover properties that we were able to see during the short time available to carry out this research. Through TGA, we were able to see that the compound began degrading around 380 °C, as shown in Figure 1. We were also able to use the TGA to verify possible spin crossover properties (The effective mass with the electromagnet on increased significantly with temperature).

The main issue that we ran into in attempts to characterize the compound was that we were unable to replicate our original TGA results. TGA results run shortly after the compound was synthesized (1-2 days) showed an increase in mass with an increase in temperature, but after waiting a couple more days (leaving the compound exposed to air overnight) these results no longer appeared.

Figure 1. Decomposition of $Co(phen)_2(NCS)_2$ in TGA

Figure 2. Possible spin crossover of $Co(phen)_2(NCS)_2$ in TGA

3.2 Computational

Our computational studies have yielded limited useful information at this stage. We initially attempted to use ORCA 4.2.1 to perform density functional theory (DFT) calculations, but were unable to obtain convergence for the self-consistent field (SCF) calculations necessary for vibrational frequency calculations. We eventually were able to obtain converged SCF calculations for structure (not vibrational calculations), but our results were still limited by the fact that we did not take into account the solid-state crystalline properties of our compound, which can affect its vibrational spectra.

To address this issue, we would need to perform additional DFT calculations using a crystal-corrected method that accounts for the solid-state nature of the compound. This

would allow us to obtain more accurate predictions of the vibrational frequencies of the compound in both its high-spin and low-spin configurations. We could also calculate the energy differences between the high- and low-spin states, which would provide insight into the factors that drive the spin crossover process.

Overall, our computational studies suggest that the cobalt-containing complex studied in this project may exhibit spin crossover properties, but further research is needed to confirm these results experimentally and to better understand the mechanisms underlying the spin crossover process. Additional computational studies that incorporate the effects of temperature and other external stimuli on the electronic structure of the compound could also provide valuable insights into its potential applications.

3.3 Discussion

One of the main challenges we faced in attempting to characterize the compound was the difficulty in reproducing our initial TGA results. When the TGA experiments were performed shortly after the compound was synthesized (1-2 days), we observed an increase in mass with an increase in temperature, which is consistent with spin crossover behavior. However, when we waited a few more days (leaving the compound exposed to air overnight) before performing the experiments again, these results were no longer observed. This may indicate that the compound degraded or changed in some way over time, which could have affected its properties.

Currently, the main limitation in our computational studies is that we were unable to obtain converged SCF calculations for vibrational frequency calculations using ORCA 4.2.1. Once we are able to obtain convergence in these calculations (hopefully updating ORCA helps us achieve this), our results will still be incorrect because we are not taking into account the solid-state properties of the material.

4 Conclusion & Further Directions

4.1 Conclusion

In conclusion, our results provide initial evidence for the potential spin crossover properties of the cobalt-containing complex $Co(phen)_2(NCS)_2$, but further research is needed to confirm these properties and to better understand the mechanisms underlying the spin crossover process. Our study highlights the challenges and limitations of the techniques used to characterize spin crossover materials and the need for further research using more advanced techniques and computational methods, as well as the difficulties inherent in working with possibly air-sensitive compounds.

4.2 Further Directions for this research

4.2.1 Experimental

Subsequent near-term research would involve further synthesis (and proper storage) of the compound, followed by TGA

analysis with electromagnet to replicate spin-crossover behavior.

The biggest challenge we ran into in the experimental section of this research is that the compound appears to be air-sensitive, and degrade on prolonged exposure to atmospheric conditions. Further studies would require us to be more careful in our handling of the compound, and make sure that an inert environment is maintained for storage whenever possible.

Another further direction of research could involve using SQUID equipment to study the magnetic properties of $Co(phen)_2(NCS)_2$. By investigating the effects of temperature and other external stimuli on the compound using SQUID measurements, we may be able to gain a deeper understanding of its spin crossover behavior and the underlying mechanisms at play. Specifically, we could try and run SQUID on our sample to determine the transition temperature and find out where the spin-crossover temperature is.

4.2.2 Computational

One possible direction for further research on $Co(phen)_2(NCS)_2$ would be to use more advanced computational methods, such as crystal-corrected density functional theory (DFT) calculations, to better understand the mechanisms underlying the spin crossover process. These calculations can provide detailed insights into the electronic structure of $Co(phen)_2(NCS)_2$ and can help identify the key factors that influence the spin crossover process.

Specifically, we hope to use ORCA 5.0.2 to obtain vibrational DFT calculations for $Co(phen)_2(NCS)_2$ to predict Raman and IR shift. Eventually, we hope to incorporate the solid-state crystal properties of the material to obtain more accurate vibrational calculations.

In addition, it would be interesting to investigate the effects of temperature and other external stimuli on the electronic structure of $Co(phen)_2(NCS)_2$ using computational methods. This could provide valuable information about how $Co(phen)_2(NCS)_2$ responds to different environmental conditions, which could be useful for applications in which the spin crossover process is used as a switch or sensor. Further research in this area could also help identify potential strategies for optimizing the performance of $Co(phen)_2(NCS)_2$ in such applications.

Overall, this line of research could contribute to a better understanding of the mechanisms behind spin crossover behavior in cobalt-containing complexes, and could have potential implications for the design and synthesis of new materials with spin crossover properties.

Supporting Information Available

All data from all instrument runs can be found at the below URL.

- https://github.com/adam-keim/CH302