The Synthesis of Spin Crossover Complexes for Covalent Attachment to Inorganic Substrates

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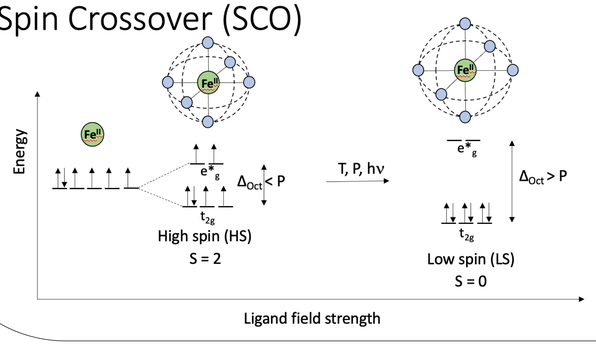
Background

Spin crossover (SCO) is observed for transition metal ions with $3d^4$-$3d^7$ electronic states. Changes in temperature, light, or pressure induce switching between the **high spin (HS)** and **low spin (LS)** states, which leads to large changes in magnetic, structural, and optical properties. This behavior is driven by variable splitting of the d-orbital pattern by molecules or ions (so-called ligands) that bond to the central metal ion. The **LS state** is favored by ligands that induce a larger splitting of d-orbitals, because under such conditions the maximum pairing of d-electrons is achieved. On the contrary, the **HS state** is favored by ligands that induce a smaller splitting, which maximizes the number of unpaired d-electrons. Taking advantage of chemistry, we aim to use a click reaction to attach Fe(II) SCO complexes to various surfaces, for potential application in electronic devices. This is a Nobel prize winning reaction between azide (N_3) and alkyne (triple bond) groups. It works under mild conditions and results in good yields of desired products. In this work, we synthesize two SCO complexes functionalized with such groups.

Spin Crossover (SCO)



Methodology

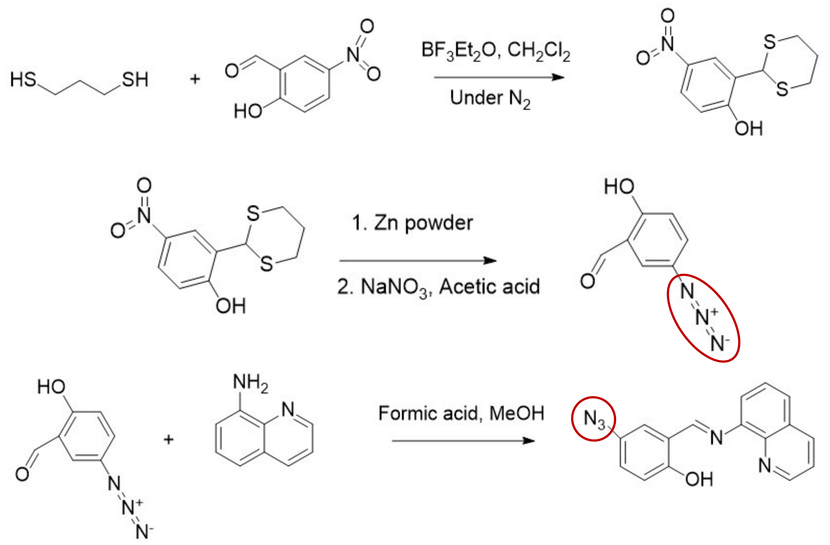
Schlenk Line

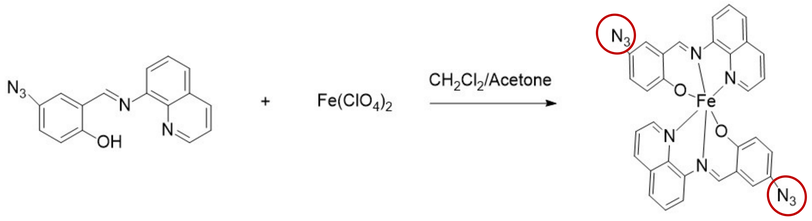
Solvent System

Single-crystal XRD

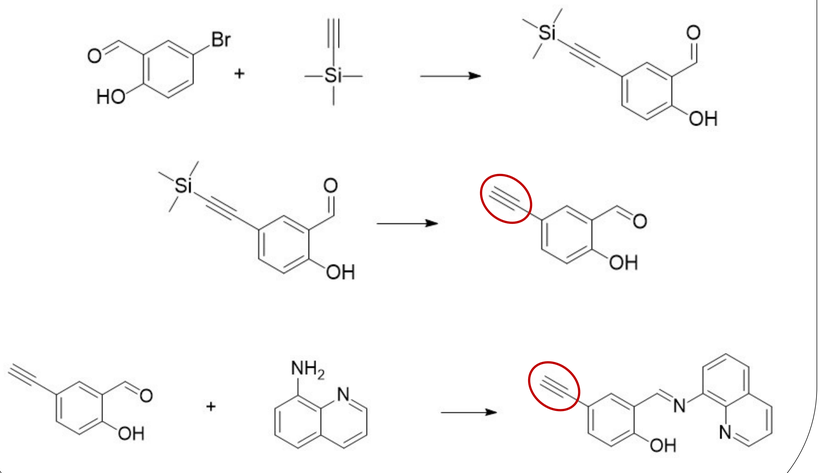
Synthesis

Azide substituent (an $-N_3$ group)

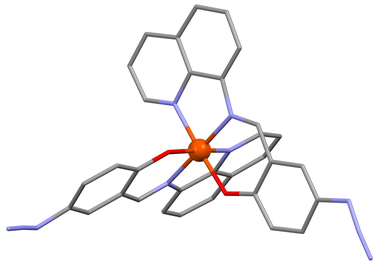


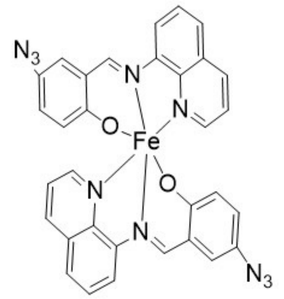


Alkyne substituent (a $-C{\equiv}CH$ group)



Crystal Structure





Temperature (K)	Fe-N (Å)	Fe-O (Å)
230	1.979	1.941

Conclusion/Results

- The azide- and alkyne-functionalized ligands have been successfully synthesized.
- Crystal structure determination has been used to confirm the structure of the azide-functionalized complex with the Fe(II) ion.
- Crystallization of a similar alkyne-functionalized complex is underway.
- Magnetic measurements will be performed on bulk samples of both complexes to verify the occurrence of spin-crossover transitions.
- If the complexes exhibit spin-crossover, they will be attached to the surface of various substrates.

References and Acknowledgments

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3. Koptur-Palenchar, J.; Gakiya-Teruya, M.; Le, D.; Shatruk, M. Zhang, X. X.; et al. *npj 2D Mater. Appl.* **2022**, *59*, 2397.

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