Single-Crystal-Single-Crystal Transformations: How Structure Affects Properties

Frank Schwandt Literature Seminar October 31, 2017

How to best detect signals has been a challenge for scientists for generations. Although conventional detectors are useful in the lab, real world situations arise in which it is useful to detect specific temperatures, pressures, or chemical species without the aid of large instrumentation. To that end, chemical sensors have shown promise for use in these applications.[1-3] A chemical sensor is a species that exhibits a change – such as color, conductivity, refractive index, mass, or temperature – when exposed to a particular stimulus. A common example of a chemical sensor is a pH indicator.

Materials that exhibit single-crystal-single-crystal (SCSC) transformations are potentially useful as chemical sensors.[4] SCSC transformations occur when a single crystal undergoes a chemical change to form a new single crystal. Examples of SCSC transformations have been shown to occur due to temperature, acidity, solvent, gases, light, pressure, and mechanical stress and are accompanied by changes in properties such as color, magnetism, dielectric constant, and heat capacity.[4-7] In this review, I will focus on SCSC materials in which the response is magnetic.

One such example of a SCSC transformation is a spin crossover transition in a coordination polymer of $Cu(hfac)_2$ and 2-(1-methyl-3-ethyl-1*H*-pyrazole-4-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl, an organic radical (Figure 1).[8]

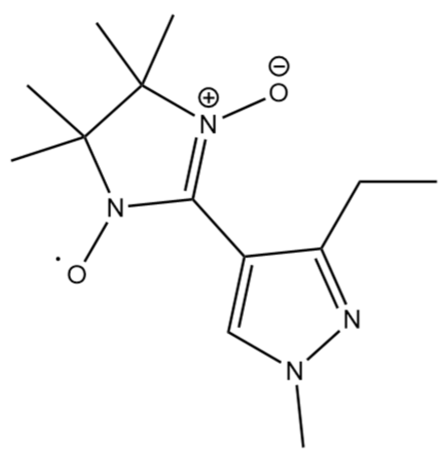

Figure 1: Structure of the organic radical 2-(1-methyl-3-ethyl-1*H*-pyrazole-4-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl.

The coordination polymer consists of alternating $Cu(hfac)_2$ and radical molecules; the lattter coordinate to the copper centers by means of both a pyrazole nitrogen and one of the NO groups of the nitronyl nitroxide. When cooled, the coordination polymer $Cu(hfac)_2L^{Me/Et}$ "depolymerizes" to form two subunits, a single-copper unit with two oxygen bound ligands ($L^{Me/Et}$-Cu-$L^{Me/Et}$) and a three-copper unit also with two ligands bridging the coppers (Cu-$L^{Me/Et}$ -Cu-$L^{Me/Et}$-Cu). This structural change (which is caused by lengthening of some of the Cu-N bonds) leads to a slight change in the effective magnetic moment. When cooled further, there is a more dramatic magnetic change from a high spin state to a low spin state in the radical-Cu-radical cluster. Upon further cooling, the radical-Cu-radical bond of the three copper subunits contracts, resulting in a switch from a high spin state to a low spin state. Unfortunately, the change in magnetic moment was still rather small and only occurred below 150 K, so it is unlikely that this system will be useful as a chemical sensor.

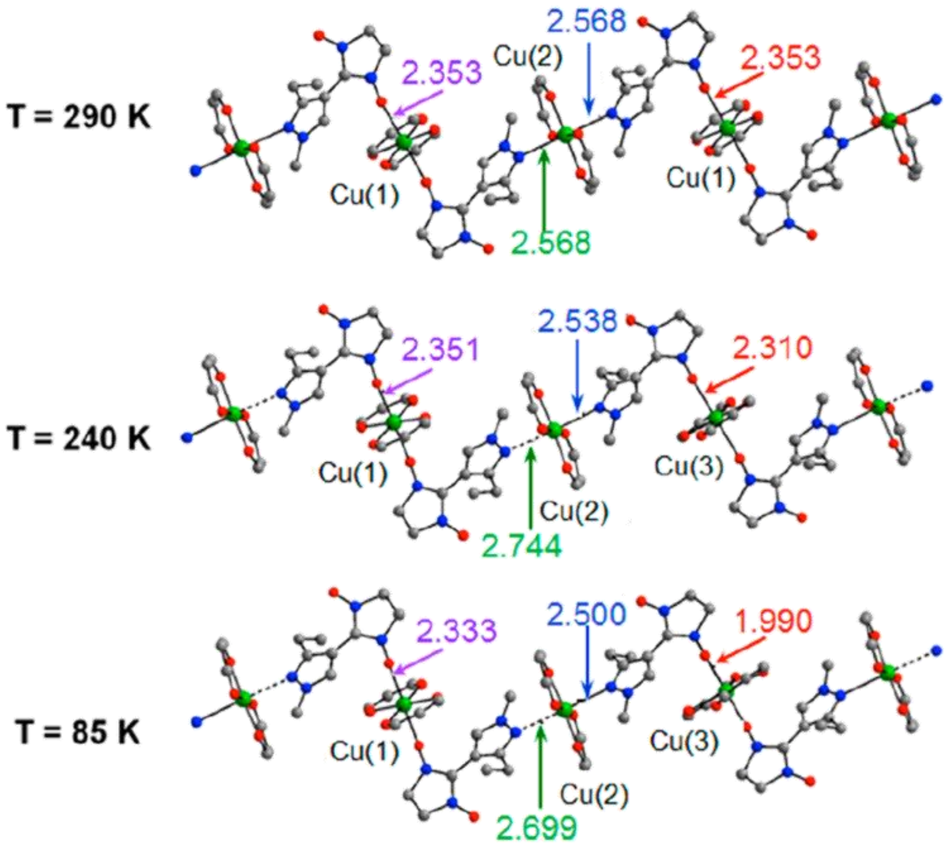

Figure 2: SCSC transformation of the coordination polymer $Cu(hfac)_2L^{Me/Et}$ which exhibits spin crossover properties

Another example of a SCSC transformation involves a material that exhibits hydration dependent magnetism (Figure 3).[9] The reaction of Co^{2+} with poly(carboxylic acid) 3,5-bis(3',5'-dicarboxylphenyl)-1*H*-1,2,4-triazole gives a layered material $[Co(H_2L)(H_2O)_2]\cdot H_2O$ in which there are two cobalt-coordinated water molecules and one water molecule present as a non-coordinated solvate. When this material is dehydrated, the solvate water and one coordinated water molecule are lost to form $Co(H_2L)(H_2O)$. This change is accompanied by a color change from red to blue. The hydrated form is paramagnetic at all temperatures (although some kind of weak ordering occurs below 16 K) whereas the dehydrated form becomes ferromagnetic below 7 K. This change in magnetic properties is caused by the formation of carboxylate bridges between two Co^{2+} centers, which has been shown to promote ferromagnetic coupling.

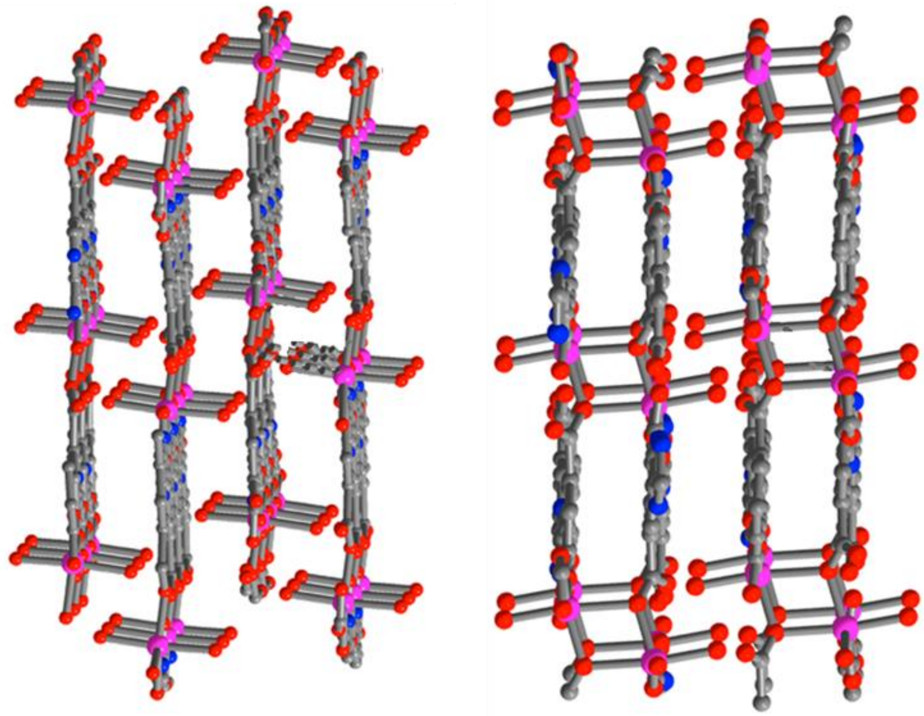

Figure 3: Crystal structures of the hydration dependent material $[Co(H_2L)(H_2O)_2]\cdot H_2O$ (left) and $[Co(H_2L)(H_2O)]$ (right)

SCSC transformations have the potential to serve as sensors, but more work is needed before they will be practical.

References

1. Wencel, D.; Abel, T.; McDonagh, C. *Anal. Chem.* **2014,** *86,* 15-29.
2. Giannoukos, S.; Brkic, B.; Taylor, S.; Marshall, A.; Verbeck, G. F. *Chem, Rev.* **2016,** *116,* 8146-8172.
3. Wenger, O. S. *Chem. Rev.* **2013,** *113,* 3686-3733.
4. Chaudhary, A.; Mohammad, A.; Mobin, S. M. *Cryst. Growth. Des.* **2017,** *17,* 2893-2910.
5. Mobin, S. M.; Mohammad, A. *Dalton Trans.* **2014,** *43,* 13032-13040.
6. Sun, J. et al. *Angew. Chem., Int. Ed.* **2011,** *50,* 7061-7064.
7. Marshal, R. J.; Griffin, S. L.; Wilson, C.; Forgan, R. S. *J. Am. Chem. Soc.* **2015,** *137,* 9527-9530.
8. Ovcharenko, V. et al. *Inorg. Chem.* **2016,** *55,* 5853-5861.
9. Hou, J.; Li, X.; Gao, P.; Sun, H.; Zhang, X. *Cryst. Growth. Des.* **2017,** *17,* 3724-3730.