

Single crystal X-ray diffraction studies of pressure-induced valence tautomerism in a cobalt-dioxolene complex

A.M. Summers¹, S.A. Boer², M.A. Hay³, F.Z.M. Zahir³, L. Goerigk³, C. Boskovic³, S.A. Moggach¹

¹The University of Western Australia, 35 Stirling Hwy, Crawley WA 6009, ²The Australian Synchrotron, 800 Blackburn Rd, Clayton VIC 3168, ³The University of Melbourne, Parkville VIC 3010
aston.summers@research.uwa.edu.au

Keywords: Single-crystal X-ray Diffraction, High-pressure, Valence Tautomerism

Molecular switches are a class of compounds characterised by the ability for a molecule to be interconverted between two or more reversible states. They have the potential for use in applications from quantum computing [1] to data storage [2]. An emerging class of molecular switches are materials displaying valence tautomerism (VT), a process in which an external stimulus, such as temperature, pressure, or light, triggers an electron transfer between a redox-active ligand and a metal centre [3]. This leads to changes in the magnetic and physical properties after switching, such as colour. VT is most commonly seen in cobalt-based metal complexes with *o*-dioxolene redox-active ligands which can exist in either the catecholate (Cat) or semiquinonate (SQ) electromer states [3]. In these cobalt complexes, upon electron transfer the species switch between a high-spin (HS) and low-spin (LS) state, leading to an overall interconversion between the LS-Co^{III}-SQ and HS-Co^{II}-Cat charge distributions [3]. In addition, this switching significantly affects the molecular structure which in turn affects the crystalline structure [4].

The investigation of VT is a relatively new field, particularly when compared to many other molecular switches such as spin-crossover materials. Yet despite the well-known impact of high-pressure on the crystalline structure of molecular crystals, of the four studies [5-8] to date investigating pressure-induced VT, no current study has elucidated changes in the crystalline structure before and after VT upon the application of high-pressure. The crystalline structure of VT and related SCO materials is important for applications in quantum computing, spintronics, and data storage, due to its role in influencing the abruptness of the spin-transition and controlling the presence of any hysteretic ability [4]. Thus, high-pressure X-ray diffraction (XRD) allows for the concurrent characterisation of VT while investigating the effects of pressure and VT upon the crystal structure. Using a diamond anvil cell (DAC) to apply pressure we were able to, for the first time, investigate structural changes during pressure-induced VT in a series of VT-active compounds. The changes in colour to the single crystal samples upon switching can be seen in Figure 1. In addition, pressure-induced VT was detected in a species which has shown to exhibit neither thermally- or photo-induced VT.



Figure 1. Colour changes in the single-crystal samples of VT active metal-complexes upon application of hydrostatic pressure using a Merrill-Bassett DAC.

- [1] Molnár, G., Cobo, S., Real, J. A., Carcenac, F., Daran, E., Vieu, C., Bousseksou, A. (2007). *Adv. Mater.* **19**, 2163-2167.
- [2] Feng, X., Mathonière, C., Jeon, I.-R., Rouzières, M., Ozarowski, A., Aubrey, M. L., Gonzalez, M. I., Clérac, R., Long, J. R., *J. Am. Chem. Soc.* 2013, 135 (42), 15880-15884.
- [3] Boskovic, C. (2013) Valence Tautomeric Transitions in Cobalt-dioxolene Complexes. *In Spin-Crossover Materials*, Halcrow, M. A., Ed. pp 315-330. Chichester: Wiley.
- [4] Halcrow, M. A. (2013) Structure:Function Relationships in Molecular Spin-Crossover. *In Spin-Crossover Materials*, Halcrow, M. A., Ed. pp 214-244. Chichester: Wiley.
- [5] Roux, C., Adams, D. M., Itie, J. P., Polian, A., Hendrickson, D. N., Verdaguer, M., (1996). *Inorg. Chem.* **35**, 2846-2852.
- [6] Caneschi, A.; Dei, A.; Fabrizi de Biani, F.; Gülich, P.; Ksenofontov, V.; Levchenko, G.; Hofer, A.; Renz, F. (2001). *Chem. Eur. J.* **7**, 3926-3930.
- [7] Li, B.; Yang, F.-L.; Tao, J.; Sato, O.; Huang, R.-B.; Zheng, L.S. (2008). *ChemComm.* **45**, 6019-6021.
- [8] Caracciolo, F., Mannini, M., Poneti, G., Pregelj, M., Janša, N., Arçon, D., Carretta, P. (2018). *Phys. Rev. B*, **98**

This work is supported by an AINSE Ltd. Postgraduate Research Award (PGRA) and an Australian Government Research Training Program Scholarship.