The Effect of High-Pressure on Molecular Magnetism

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Polynuclear clusters of paramagnetic metal ions have attracted intense study since the discovery that such molecules can display the phenomenon of single-molecule magnetism.[1] The energy barrier to the relaxation of the magnetisation implies a large ground state spin multiplicity (*S*) and a significant zero-field splitting (*D*) of that ground state. The strength of coupling and the magnitude of the zero-field splitting are governed by the molecular geometry. Here we show that the application of hydrostatic pressure can significantly change the intra-molecular bond lengths and angles – and in some cases the connectivity - in a host of molecular or molecule-based complexes and in-so-doing greatly modify the observed magnetic parameters.[2-6]

Two 'Mn_6' SMMs, hydroxo-bridged Cu and oxo-bridged Mn dimers can all be structurally and magnetically distorted by pressure. We describe the combined high pressure crystallographic and high pressure magnetism experiments performed on these materials.

References:

1. Sessoli, R.; Tsai, H.-L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N., High-Spin Molecules: $[Mn_{12}O_{12}(O_2CR)_6(H_2O)_4]$. *J. Am. Chem. Soc.* **1993,** 115, 1804-1816.
2. Prescimone, A.; Milios, C. J.; Moggach, S. A.; Warren, J. E.; Lennie, A. R.; Sanchez-Benitez, J.; Kamenev, K.; Bircher, R.; Murrie, M.; Parsons, S.; Brechin, E. K., $[Mn_6]$ under pressure: a combined crystallographic and magnetic study. *Angew. Chemi. Int. Ed.* **2008,** 47, (15), 2828-2831.
3. Prescimone, A.; Milios, C. J.; Sanchez-Benitez, J.; Kamenev, K.; Loose, C.; Kortus, J.; Moggach, S. A.; Murrie, M.; Warren, J. E.; Lennie, A. R.; Parsons, S.; Brechin, E. K., High pressure induced spin changes and magneto-structural correlations in hexametallic SMMs. *Dalton Transactions* **2009**, 4858–4867.
4. Prescimone, A.; Sanchez-Benitez, J.; Kamenev, K.; Moggach, S. A.; Murrie, M.; Warren, J. E.; Lennie, A. R.; Parsons, S.; Brechin, E. K., High pressure effects on a trimetallic MnII/III SMM. *Dalton Transactions* **2009**, 7390-7395.
5. Prescimone, A.; Sanchez-Benitez, J.; Kamenev, K.; Moggach, S. A.; Warren, J. E.; Lennie, A. R.; Parsons, S.; Brechin, E. K., High pressure studies of hydroxo-bridged Cu(II) dimers. *Dalton Transactions* **2010**, (1), 113-123.
6. Prescimone, A.; Sanchez-Benitez, J.; Kamenev, K.; Moggach, S. A.; Warren, J. E.; Lennie, A. R.; Murrie, M.; Parsons, S.; Brechin, E. K., High Pressure study of oxo-bridged mixed-valent Mn3/Mn4 dimers. *Z. Naturforsch. B* **2010,** 65b, (3), 221 – 230.