Title:
The influence of the axial ligand, X, on the electronic structure of the Co3(dpa)4X2 extended metal atom chains

Abstract:
The extended metal atom chains have received a lot of interest in the field of molecular electronics. Consisting of a linear chain of at least three metal atoms with two terminal axial ligands and surrounded by a spiralling polydentate organic ligand they resemble the structure of a macro wire. Many different metals have been studied. The tricobalt complex is perhaps the most interesting, exhibiting two stable structures either symmetric (equal length Co-Co bonds) or asymmetric (unequal Co-Co bonds) in the metal core and an associated spin crossover. [1] A thorough examination of the Co3(dpa)4Cl2 (dpa=2,2'-dipyridylamide) compound has been undertaken by this group in the past. Three electronic states were proposed to explain the experimental results. A doublet ground state, 2A (C2 symmetry), a high spin quartet state, 4B, and a flat surfaced doublet, 2B, bridging the high-energy region between the two allowing the observed continuous variation in the properties. [2] Extending the series to the fluoride, bromide and iodide counterparts this computational study examines the electronic mechanisms by which the symmetric-unsymmetric and low spin-high spin balances are determined under the influence of the axial ligands.

[1] R.Clérac, F. A. Colon, L. M. Daniels, K. R. Dunbar, K. Kirschbaum, C. A. Murillo, A. A. Pinkerton, A. J. Schultz & X. Wang, J. Am. Chem. Soc., 2000, 122 (26), 6226–6236
[2] D. A. Pantazis & J. E. McGrady, J. Am. Chem. Soc., 2006, 128 (12), 4128□-4135