



Organic-based Magnets: New Chemistry and New Materials for This Millennium



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Organic-based materials exhibiting the technologically important property of bulk magnetism have been pioneered in our laboratory and studied in collaboration with many research groups worldwide. These magnets are prepared via conventional organic synthetic chemistry methodologies, but unlike classical inorganic-based magnets do not require high-temperature metallurgical processing. Furthermore, these magnets are frequently soluble in conventional organic solvents and have saturation magnetizations more than twice that of iron metal on a mole basis, as well as in some cases coercive fields exceeding that of all commercial magnets (e.g., Co₅Sm). Also several magnets with critical temperatures (T_c) exceeding room temperature have been prepared. In addition to an overview of magnetic behavior, numerous examples of structurally characterized magnets made from molecules will be presented. Four examples magnetically order above room temperature and as high as 127 °C.

These will include $[M^{III}(C_5Me_5)_2][A]$, $[Mn^{III}(\text{porphyrin})][A]$ ($A = \text{cyanocarbon etc. electron acceptors}$) as well as $M[\text{TCNE}]_x$ (TCNE = tetracyanoethylene), which for $M = V$ is a room temperature magnet that can be fabricated as a thin film magnet via Chemical Vapor Deposition (CVD) techniques. A newer class of magnets of $[\text{Ru}_2(\text{O}_2\text{CR})_4]_3[\text{M}(\text{CN})_6]$ ($M = \text{Cr, Fe; R} = \text{Me, } t\text{-Bu}$) composition will also be discussed. For $R = \text{Me}$ an interpenetrating, cubic (3-D) lattice forms and the magnet exhibits anomalous hysteresis, saturation magnetization, out-of-phase, $\chi''(T)$, AC susceptibility, and zero field cooled-field cooled temperature-dependent magnetization data. This is in contrast to $R = t\text{-Bu}$, which forms a layered (2-D) lattice. Additionally, new magnets possessing the nominal Prussian blue composition, $M[\text{M}(\text{CN})_6]_x$ and $(\text{Cation})_y\text{M}[\text{M}(\text{CN})_6]$, but not their structure, will be described. This forms a series of cation-adaptive structures with $[\text{NEt}_4]_2\text{Mn}_3(\text{CN})_8$, $[\text{NEt}_4]\text{Mn}_3(\text{CN})_7$, $[\text{NMeEt}_3]_2\text{Mn}_5(\text{CN})_{12}$ and $[\text{NMe}_4]_3\text{Mn}_5(\text{CN})_{13}$ stoichiometries that order as antiferromagnets or ferrimagnets. Finally, $\text{Li}[\text{TCNE}]$ magnetically orders as a weak ferromagnet (= canted antiferromagnet) below 21.0 K. The structure, determined ab initio from synchrotron powder X-ray diffraction data, consists of a planar $\mu_4\text{-}[\text{TCNE}]^-$ bound to four tetrahedral Li^+ ions with two interpenetrating diamondoid sublattices, with closest inter-lattice separations of 3.43 and 3.48 Å. At 5 K this magnetic state is characterized by a coercivity of ~30 Oe, 10 emuOe/mol remnant magnetization, and a canting angle of 0.5°.

The structure, DC magnetization at ambient and applied pressure, as well as the AC susceptibility at ambient pressure in addition to the computational analysis of the magnetic couplings will be presented. New physics observed from examples of organic-based magnet will be discussed.