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Coordination polymers incorporating weakly coordinating fluoroanions

Robert C. Thompson

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia V6T 1Z1, Canada

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Studies of polymeric complexes of the transition metals incorporating weakly coordinating fluoroanions as bridging or ancillary ligands have permitted examination of the effects of electronic factors on the structures and properties of coordination polymers. Iron(II) sulfonates of composition $Fe(RSO_3)_2$ are considered to have extended sheet structures with metals linked by bridging sulfonate groups. There is evidence for antiferromagnetic exchange in these systems and, moreover, for a significant reduction in the strength of the exchange when, for example, $R = CH_3$ is replaced by $R = F$ or CF_3. Lack of detailed structural information on these systems has, however, limited our understanding of them [1]. Better magneto-structural correlations have been obtained for 1,4-diazine (pyrazine, pyz) bridged complexes of Fe^{II} and Cu^{II} incorporating CH_3SO_3 or CF_3SO_3 groups [2]. This work has provided evidence that, with the more weakly coordinating CF_3SO_3, antiferromagnetic exchange via the diazine ligand is slightly enhanced due to stronger metal–diazine interactions. By employing fluoroanions as ancillary ions, we have explored some possibilities of synthesizing novel cationic polymeric lattices. Several such diazine-bridged copper(I) complexes have now been isolated including $Cu(pyz)_2(CF_3SO_3)$, which has an extended chain structure [3], $[Cu_2(dmpyz)_3][PF_6]_2$ (dmpyz = 2,5-dimethylpyrazine), which has a graphite-related sheet structure [4],and $Cu(dmpyz)_2][PF_6]$, which has a diamond-related three-dimensional lattice [4].

Binary transition metal dialkyl- and diaryl-phosphinates are known to form extended linear chain polymeric structures and many exhibit interesting magnetic properties; however, little is known about the fluorinated derivatives. In work in progress [5], the acids $CF_3(CF_2)_3(CH_2)_2PO_2H$ and $(C_6F_5)_2PO_2H$, and their corresponding copper(II) derivatives have been synthesized. The structure of the monohydrate of perfluorodiphenylphosphinic acid has also been obtained by single crystal X-ray diffraction methods. Comparisons of the magnetic properties of the copper compounds with those of the perhydro analogues reveal differences. Whereas, for example, copper(II) diphenylphosphinate exhibits weak ferromagnetic exchange [6], the fluorinated analogue is antiferromagnetic. This appears to be caused by a change in the CuO_4 chromophore from square planar in the diphenyl compound to a distorted tetrahedral coordination in the fluorinated analogue. The difference between the two n-hexyl compounds is less dramatic. Both are weakly ferromagnetic and appear to have similar pseudo-tetrahedral coordination geometries about the metal centers. The magnetic properties suggest, however, a more regular geometry in the case of the fluorinated derivative.

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