ABSTRACT

Cobalt(II) and Manganese(II) complexes of monosubstituted ligands: Assessment of the electronic and magnetic properties of their polymers.

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Attempts were made to synthesise Co(II) and Mn(II) complexes of a variety of monosubstituted squarate ligands, in order to investigate the coordinating properties of the ligands and the effect of the substituent on the extent of metal-metal interactions, and so produce a prototype for the synthesis of complexes exhibiting semiconductivity and molecular magnetism.

Complexation of the dialkylaminosquarate ligands with Co(II) resulted in the hydrolysis of the amino substituent but, for Mn(II), the metal squarate and a small amount of the salt, $[Mn(H_2O)_6][C_4O_3NH_2]_2 \cdot 2H_2O$ were produced indicating that the hydrolysis was not complete. Although hydrolysis of the substituent also occurred when the tetraalkylammonium salts of the dialkylaminosquarate ligands were used, with dimethylformamide (dmf) as solvent, the chain polymers $\{M(\mu\text{–}C_4O_4)(OH_2)_2(dmf)_2\}_n$ [M = Mn; Co] were produced.

The methylsquarate and phenylsquarate ligands which contained substituents that were not easily hydrolysable, produced Co(II) and Mn(II) complexes when reacted with the appropriate metal salt. The monomers $M(CH_3C_4O_3)_2(H_2O)_4$ [M = Co, Mn], exist as corrugated sheets, whilst $\{[Co(\mu\text{–}CH_3C_4O_3)(H_2O)_4][NO_3]\cdot 2H_2O\}_n$ exists as a polymeric chain. The manganese(II) phenylsquarate $[Mn(\mu\text{–}C_6H_5C_4O_3)(C_6H_5C_4O_3)(H_2O)_3]_n$ exists as a linear polymer and the cobalt(II) phenylsquarate as a monomer. The polymeric species did not exhibit semiconductivity and molecular magnetism since the ligand groups did not possess sufficient electron density to mediate any significant exchange interactions.

Complexation of Co(II) and Mn(II) with tetrabutylammonium 3-methoxycyclobut-3-ene-1,2-dionate(1-), a ligand having a monosubstituent with lone pair electrons that could effectively migrate unto the ring, produced monomers due to a *cis* directing effect of the monosubstituent.

Keywords: Hazel-Ann Hosein; monosubstituted squarates; transition metal complexes; semiconductivity; variable temperature magnetochemistry.