ABSTRACT

The synthesis, characterisation and physico-chemical analysis of selected metal complexes with monosubstituted squarate ligands.

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In order to investigate the coordinating properties of a variety of monosubstituted squarate ligands and the effects of the substituents on the extent of metal–metal interactions in their complexes, the synthesis of a number of such compounds was undertaken.

With the sterically demanding diphenylaminosquarate ligand the polymeric copper complex $\{Cu[\mu-(C_6H_5)_2NC_4O_3]_4(H_2O)_2\}_n$ is produced, whilst the lanthanide counterparts are either monomeric or dimeric. In an attempt to synthesise polymeric lanthanide complexes, monosubstituted squarate ligands with less sterically demanding substituents, namely methylsquarate and phenylsquarate, were used. The lanthanum(III) methylsquarate $\{[La(\mu_3-C_4O_3CH_3)_2(H_2O)_6]Cl_2\cdot H_2O\}_n$ exists as polymeric sheets, the europium(III) methylsquarate $\{Eu(\mu-C_4O_3CH_3)_6(H_2O)_2\}_n$ as three dimensional cages, and the europium(III) phenylsquarate $\{Eu(\mu-C_6H_5C_4O_3)_2(C_6H_5C_4O_3)_2(H_2O)_2(CH_3OH)_2\cdot CH_3OH\}_n$ as one dimensional polymeric chains.

Spectroscopic and crystallographic analyses provide evidence for multiple bond localisation within the ligand C_4–cycle in a number of these metal complexes. In addition, these analyses confirm the migration of the nitrogen lone pair onto the squarate ring in the metal complexes synthesised with the diphenylaminosquarate ligand.

Luminescence studies performed on europium(III) squarate, europium(III) phenylsquarate and europium(III) diphenylaminosquarate revealed that the europium(III) diphenylaminosquarate complex exhibits a bright red emission at 77 K but does not emit at room temperature while the europium(III) phenylsquarate luminesces both at room temperature and at 77 K. The emission exhibited by europium(III) phenylsquarate is apparently sensitised by the phenyl substituent, which is directly attached to the squarate ring. A comparison of the luminescence properties of the europium(III) squarate, europium(III) phenylsquarate and europium(III) diphenylaminosquarate complexes show emissions dominated by the $Eu^{3+}(^5D_0 \rightarrow {}^7F_j)$ transitions. The temperature dependence of their luminescence reveals strong Eu···Eu interactions, which keep the energy transport process in the dynamic regime.

Keywords: Bert Dale Alleyne; monosubstituted squarates; transition metal complexes; lanthanide complexes; luminescence spectroscopy.