ABSTRACT

Investigations of chiral precursors for synthesis of novel monosubstituted squarate complexes

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Attempts were made to synthesise selected transition metal complexes of a variety of monosubstituted squarate ligands, in order to investigate their suitability as chiral precursors for the synthesis of novel monosubstituted squarate complexes.

Reaction of 3-hydroxy-4-[(1′S,2′R)-(2′-hydroxy-1′,2′-diphenylethyl)amino] cyclobut-3-ene-1,2-dione and 3-hydroxy-4-[(1′R,2′S)-(2′-hydroxy-1′,2′-diphenylethyl)amino]cyclobut-3-ene-1,2-dione with selected first row transition metals produced five novel monosubstituted squarate complexes whose structural properties were elucidated by single crystal X-ray analysis. Monomeric aminosquarate complexes, instead of the intended target complexes of the chiral ligands, were obtained due to the fragmentation of the chiral substituents on these ligands via a metal-mediated S_N1 type hydrolysis.

Attempts to solve the problem of the non-complexation of the chiral monosubstituted squarate ligands were made by using their sodium salts instead of the non-ionised counterparts. The approach was intended to enhance their ligating capabilities since it is well established that the ionic forms of ligands possess a superior coordinating capability to their non-ionised parent molecules. However, reaction of *cis*-$[\mathrm{RuCl_2(dmso)_4}]$ with the sodium salt of the 3-hydroxy-4-[(1′S,2′R)-(2′-hydroxy-1′,2′-diphenylethyl)amino]cyclobut-3-ene-1,2-dione and 3-hydroxy-4-[(1′R,2′S)-(2′-hydroxy-1′,2′-diphenylethyl) amino]cyclobut-3-ene-1,2-dione resulted in the formation of a sodium bridged polymer, [Na] [*fac*-$\mathrm{RuCl_3(dmso)_3]\cdot H_2O}$ suggesting that the formation of the salt competes with the desired complexation reaction.

Complexation of 3-[(S)-(1′-benzyl-2-hydroxyethyl)amino]-4-hydroxycyclobut-3-ene-1,2-dione with *cis,fac*-$[\mathrm{RuCl_2(dmso)_3(3,5\text{-}lut)}]$ and $\mathrm{Eu(NO_3)_2\cdot 6H_2O}$ resulted in the formation of $\{$*fac*-$[\mathrm{(Cl)(dmso)_3Ru(\mu\text{-}C_2O_4)}]\}_2$ and europium squarate, $[\mathrm{Eu(C_4O_4)_2(H_2O)_4}]$ respectively.

The formation of [Na][*fac*-$\mathrm{RuCl_3(dmso)_3]\cdot H_2O}$, $\{$*fac*-$[\mathrm{(Cl)(dmso)_3Ru(\mu\text{-}C_2O_4)}]\}_2$ and $[\mathrm{Eu(C_4O_4)_2(H_2O)_4}]$ instead of the corresponding complexes of the monosubstituted squarate ligands resulted from a metal–mediated $\mathrm{S_N2}$ type hydrolysis of the ligand substituent in each case.

Keywords: Shireen Seenarine; monosubstituted squarates; transition metal complexes.