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 SN1 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-[RuCl₂(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-RuCl₃(dmso)₃]·H₂O 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-[RuCl₂(dmso)₃(3,5-lut)] and Eu(NO₃)₂·6H₂O resulted in the formation of {fac-[(Cl)(dmso)₃Ru(μ-C₂O₄)]}₂ and europium squarate, [Eu(C₄O₄)₂(H₂O)₄] respectively.

The formation of [Na][fac-RuCl₃(dmso)₃]·H₂O, {fac-[(Cl)(dmso)₃Ru(μ-C₂O₄)]}₂ and [Eu(C₄O₄)₂(H₂O)₄] instead of the corresponding complexes of the monosubstituted squarate ligands resulted from a metal–mediated Sₘ₂ type hydrolysis of the ligand substituent in each case.

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