

ABSTRACT

Synthesis, Characterisation and Testing of Metal Complexes of Monosubstituted Squarate Ligands for Electronic and Biomedical Properties

Patrice Michala Treacle Piggot

The reactions of *cis*-[RuCl₂(dms_o)₄], and selected first row transition metal and lanthanide salts separately with a variety of monosubstituted squarate ligands produced several novel compounds, whose structural properties were elucidated by single crystal X-ray analysis, and whose electronic and biomedical properties were assessed where applicable.

Complexation of one such monosubstituted squarate ligand – anilinosquarate – with selected first row transition metals produced isomorphous polymers: $\{M(\mu\text{-C}_6\text{H}_5\text{NHC}_4\text{O}_3)_2(\text{CH}_3\text{OH})_2\}_n$ (M = Mn, Co, Cu, Zn); $\{M(\mu\text{-C}_6\text{H}_5\text{NHC}_4\text{O}_3)_2(\text{H}_2\text{O})_2\}_n$ (M = Mn, Cu); and a monomer $[\text{Ni}(\text{C}_6\text{H}_5\text{NHC}_4\text{O}_3)_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$. However, for the lanthanides, the neutral polymers: $\{\text{La}_2(\mu_2\text{-C}_4\text{O}_4)_3(\text{H}_2\text{O})_{11} \cdot 2\text{H}_2\text{O}\}_n$; $\{\text{Sm}(\mu\text{-C}_6\text{H}_5\text{NHC}_4\text{O}_3)_3(\text{H}_2\text{O})_4 \cdot 3\text{H}_2\text{O}\}_n$; $\{\text{Sm}(\text{C}_6\text{H}_5\text{NHC}_4\text{O}_3)(\mu_3\text{-C}_4\text{O}_4)(\text{H}_2\text{O})_4 \cdot \text{H}_2\text{O}\}_n$; $[\{(\text{C}_6\text{H}_5\text{NHC}_4\text{O}_3)_2(\text{H}_2\text{O})_5\text{Yb}\}_2(\mu\text{-C}_4\text{O}_4)] \cdot 4\text{H}_2\text{O}\}_n$; and the ionic polymers $\{[\text{Ln}(\text{C}_4\text{O}_4)(\text{H}_2\text{O})_6][\text{C}_6\text{H}_5\text{NHC}_4\text{O}_3] \cdot 4\text{H}_2\text{O}\}_n$ (Ln = Eu, Gd, Tb, Er, Yb) were formed. For the first row transition metals, coordination of the anilinosquarate ligand occurred in all cases with no evidence of hydrolysis of this ligand. However, for the lanthanides, coordination and/or hydrolysis occurred depending on the identity of the metal.

Magnetochemical analysis revealed normal paramagnetic behaviour for $\{\text{Mn}(\mu\text{-C}_6\text{H}_5\text{NHC}_4\text{O}_3)_2(\text{CH}_3\text{OH})_2\}_n$, and weak ferromagnetic interactions for $\{\text{Cu}(\mu\text{-C}_6\text{H}_5\text{NHC}_4\text{O}_3)_2(\text{CH}_3\text{OH})_2\}_n$ and $\{\text{M}(\mu\text{-C}_6\text{H}_5\text{NHC}_4\text{O}_3)_2(\text{H}_2\text{O})_2\}_n$ (M = Mn, Cu) due to low electron density on the distorted C₄-cycle in the anilinosquarate ligand in these complexes.

Reaction of the *p*-anisolesquarate ligand with a series of Ln(III) ions produced the polymeric complexes: $\{\text{Ln}(\mu\text{-CH}_3\text{OC}_6\text{H}_5\text{C}_4\text{O}_3)(\text{CH}_3\text{OC}_6\text{H}_5\text{C}_4\text{O}_3)_2(\text{H}_2\text{O})_4 \cdot x\text{H}_2\text{O}\}_n$ (Ln = La, Eu, Gd); $\{(\text{CH}_3\text{OC}_6\text{H}_5\text{C}_4\text{O}_3)_3\text{Tb}(\text{H}_2\text{O})_4(\mu\text{-CH}_3\text{OC}_6\text{H}_5\text{C}_4\text{O}_3)(\text{CH}_3\text{OC}_6\text{H}_5\text{C}_4\text{O}_3)_2\text{Tb}(\text{H}_2\text{O})_5\} \cdot \text{H}_2\text{O}$, whose tertiary structures changed subtly with decreasing ionic size of the metal. The unexpected formation of salts: $[\text{M}(\text{H}_2\text{O})_6][\text{CH}_3\text{OC}_6\text{H}_5\text{C}_4\text{O}_3]_2$ (M = Mn, Co, Ni, Zn) instead of coordination of this ligand with the first row transition metals was apparently due largely to the stabilisation of the tertiary structures of these salts by hydrogen-bonding. Unlike the *p*-anisolesquarate ligand, the analogous *o*-anisolesquarate actually formed coordination compounds: $[\text{M}(\text{CH}_3\text{OC}_6\text{H}_5\text{C}_4\text{O}_3)_2(\text{H}_2\text{O})_4]$ (M = Cu, Zn), most likely due to a reduced number of hydrogen bonding interactions.

The ruthenium(II) monosubstituted squarate complexes *fac*-[Ru(Cl)(dmsO)₃(H₂O)(L)]·xH₂O (L = CH₃OC₆H₅C₄O₃, C₆H₅NHC₄O₃) and *fac*-[Ru({C₆H₅})₂NC₄O₃](Cl)(dmsO)₃(H₂O)]·C₄H₈O were obtained by reacting *cis*-[RuCl₂(dmsO)₄] with the appropriate monosubstituted squarate ligand. These all exhibited hydrogen-bonding while the diphenylamino and anilino analogues also showed π-stacking. Initial attempts which failed to produce ruthenium(II) monosubstituted squarate complexes resulted in the synthesis of novel ruthenium complexes: *cis, fac*-Ru(CH₃CN)Cl₂(dmsO)₃; {*cis*-[(CH₃CN)(Cl)

$(\text{dmso})_2\text{Ru}(\mu\text{-C}_2\text{O}_4)]\}_2$; $\{\text{fac-}[(\text{Cl})(\text{dmso})_3\text{Ru}(\mu\text{-C}_2\text{O}_4)]\}_2$; among others. Cytotoxicity tests on three of the Ru complexes synthesised showed only a mild antiproliferative effect with low selectivity.

Keywords: Patrice Michala Treacle Piggot; monosubstituted squarate ligands; transition metal complexes; lanthanide complexes; electronic properties; biomedical properties.