

Tuning the reactivity of ruthenium(II) terpyridyl complexes using auxiliary ligands: kinetic and mechanistic studies

Abstract

Substitution behavior of the labile aqua ligand in four mononuclear ruthenium(II) terpyridyl complexes with different auxiliary N (pyridine) (**Ru1**), N^N (2,2'-bipyridyl (**Ru2**), 2'-(2-pyridyl)quinoline (**Ru3**), 2,2'-biquinoline (**Ru4**) ligands was investigated using three nucleophiles; thiourea, 1,1-dimethylthiourea and 1,1,3,3-tetramethylthiourea. The effect of concentration and temperature on the substitution behavior of the complexes were studied under *pseudo*-first order conditions using UV–Vis spectrophotometer. The second order rate constants (k_2) of the aqua complexes decreased in the order: **Ru4** > **Ru3** > **Ru1** > **Ru2**. The results showed that the rate of substitution of the aqua ligand increased with an increase in the π -surface area of the N^N bidentate auxiliary ligands. This is attributable to an upsurge in π -back-donation and electrophilicity of the complexes as the π -extension of the auxiliary ligands increases. **Ru2** is less reactive than **Ru1** due to the increased steric hinderance introduced by the 2,2'-bipyridyl bidentate auxiliary ligand in **Ru2** compared to **Ru1** which has two independent *trans* pyridines. From computational results, it was observed that as the aromatic surface area of the auxiliary ligand increased from **Ru1**–**Ru4**, the HOMO–LUMO gap decreased accordingly. Consequently, the chemical softness and electrophilicity of the complexes increased accordingly. This is corroborated by the decrease in pKa values of the complexes as one moves from **Ru1** to **Ru4**. As a result, the nucleophilic attack becomes facile from **Ru1** to **Ru4**. All the reactions follow an associative interchange mechanism as indicated by the positive activation enthalpy and negative activation entropy. The crystal structure of bipyridylterpyridylthiourearuthenium(II) perchlorate show that the substitution product obtained is stable.

Authors:

- [Gershom Kyalo Mutua](#),
- [Meshack Sitati](#),
- [Daniel O. Onunga](#),
- [Deogratius Jaganyi](#) &

- [Allen Mambanda](#)