Understanding the electronic and π-conjugation roles of quinoline on ligand substitution reactions of platinum(II) complexes

Author(s)
Grace Kinunda,
Deogratius Jaganyi

Abstract

A kinetic and mechanistic study of chloride substitution by thiourea nucleophiles, namely thiourea, *N*-methylthiourea, *N*,*N*-dimethylthiourea and *N*,*N*,*N*′,*N*′-tetramethylthiourea in the complexes chlorobis-(2-pyridylmethyl)amineplatinum(II) (Pt1), chloro *N*-(2-pyridinylmethyl)-8-quinolinamineplatinum(II) (Pt2), chloro *N*-(2-pyridinylmethylene)-8-quinolinamineplatinum(II) (Pt3) and chlorobis(8-quinolinyl)amineplatinum(II) (Pt4) was undertaken under *pseudo*-first-order conditions using UV–visible spectrophotometry. The study showed that lability of the chloro leaving group is dependent on the strength of π-interactions between the filled $d\pi$-orbitals of the metal and the empty π*-orbitals of the chelating ligand in the following manner: Pt1 > Pt3 > Pt2 > Pt4. Introduction of the quinoline moiety within the non-labile chelated framework of the Pt(II) complexes results in a more electron-rich metal centre which retards the approach of the nucleophile through repulsion. Moreover, the net σ-effect of the ligand moiety plays a significant role in controlling the reactivity of the complexes. The experimental results are interpreted with the aid of computational data obtained by density functional theory (B3LYP(CPCM)/LANL2DZp//B3LYP/-LANL2DZp) calculations. The mode of substitution remains associative as supported by negative entropies and the dependence of the second-order rate constants on the concentration of entering nucleophiles.