A kinetic study of aqua ligand substitution in dinuclear Pt(II) complexes containing four non-coplanar pyridine ligands

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Abstract
Substitution reactions of the aqua ligands from azine-bridged dinuclear platinum(II) complexes of the type [{*cis*-$Pt(py)_2(OH_2)$}$_2$(μ-pzn)]$(ClO_4)_4$ [pzn = pyrazine (**Pt-PZN**), 2,3-dimethylpyrazine (**Pt-2,3PZN**), 2,5-dimethylpyrazine (**Pt-2,5PZN**) or 2,6-dimethylpyrazine (**Pt-2,6PZN**)] by thiourea nucleophiles were investigated under *pseudo* first-order conditions as a function of concentration and temperature using the stopped-flow technique. The experimental results are discussed in reference to structures obtained by DFT calculations. The results are in good agreement with the p*K*a values of the complexes as well as DFT calculations. Compared to [{*cis/trans*-$Pt(NH_3)_2(OH_2)$}$_2$(μ-pzn)]$(ClO_4)_4$, the complexes in this series react faster by a factor of 10 or 23 respectively due to the presence of pyridine rings, which forces the geometry to allow π-back bonding to take place such that the electrons from the metal centres are accepted to the empty π^*-orbitals of the pyridine subunits. The reactivity of the nucleophile is sterically dependent, with *N*,*N*,*N*′,*N*′-tetramethylthiourea reacting three times slower than thiourea. In all complexes and for both substitution steps, the mode of activation remains associative in nature.