

ORIGINAL PAPER

Reactivity of base catalysed hydrolysis of 2-pyridinylmethylen-8-quinolinyl-Schiff base iron(II) iodide complexes: solvent effects

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Three ligands of 2-pyridinylmethylen-8-quinolinyl (L1), methyl-2-pyridinylmethylen-8-quinolinyl (L2), and phenyl-2-pyridinylmethylen-8-quinolinyl (L3), Schiff bases were synthesised by direct condensation of 8-aminoquinoline with 2-pyridinecarboxaldehyde, 2-acetylpyridine, or 2-benzoylpyridine. They coordinated to Fe(II) ion in a 1 : 2 mole ratio followed by treatment with iodide ions affording complexes with a general formula $[\text{Fe}(\text{L})_2]\text{I}_2 \cdot 2\text{H}_2\text{O}$, ($\text{L} = \text{L1, L2, or L3}$). Spectrophotometric evaluation of the kinetics of base catalysed hydrolysis of these complex cations was carried out with an aqueous solution of NaOH in different ratios of water/methanol binary mixtures. Kinetics of the hydrolysis followed the rate law $(k_2[\text{OH}^-] + k_3[\text{OH}^-]^2)[\text{complex}]$. Reactivity trends and their rate constants were compared and discussed in terms of ligand structure and solvation parameters. The methanol ratio affects the hydrolysis as a co-solvent which was analysed into initial and transition state components. The increase in the rate constant of the base hydrolysis of Fe(II) complexes, as the ratio of methanol increases, is predominantly caused by the strong effect of the organic co-solvent on the transition states.

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Introduction

Schiff bases have been one of the most important chemicals categories for over ten decades due to their simple synthesis and complexing ability. Literature shows that the study of this diverse ligand system is linked with many key advances in inorganic chemistry (Zhang et al., 1990; Tisato et al., 1994; Lacroix, 2001). Transition metal complexes of Schiff bases do not only play a major role in the development of modern coordination chemistry, they are also involved in inorganic biochemistry, catalysis, enzymatic reactions (Zhang et al., 1990), biological activities (Prashanthi et al., 2008; Daniel et al., 2008; Galal et al., 2009), optical materials and thin films (Lacroix, 2001), magnetism, and molecular architecture (Ray et al., 2003, 2005; Lippard & Berg, 1994;

Holm et al., 1996; McGuinness et al., 2003; Lin & Kagan, 2003).

Transition metal complexes, particularly iron-Schiff base complexes, analogous to those of porphyrins obtained by Fujii and Funahashi (2002) are important for the catalytic asymmetric oxidation of alcohols and alkenes (Bryliakov & Talsi, 2004; Katsuki, 2004). These complexes have wide applicability in many fields of photo-, magneto- (Haikarainen et al., 2001; Yang et al., 2006; Ferbinteanu et al., 2005), and electrochemistry (Sen et al., 2006; Júnior et al., 2004). Intensive fundamental chemical research on Fe(II) Schiff base complexes has not been done yet (Shaker et al., 2003).

The base catalysed hydrolysis reaction for 3d transition metal complexes has been extensively studied for some decades (Jackson & Sargeson, 1980; Jack-

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