

## Effect of non-leaving ligand environment on aqua ligand substitution in chromium(III) Schiff-base complexes

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A series of new Schiff-base complexes of chromium(III) of the general formulation,  $\text{Cr}(\text{Schiff-base})(\text{H}_2\text{O})_2^+$ , where Schiff-base = 1,2-*bis*(salicylideneamino)ethane (salen), 1,3-*bis*(salicylideneamino)propane (salprn) and 1,4-*bis*(salicylideneamino)butane (salbuen) have been prepared and characterized. The single crystal X-ray diffraction study of *trans*- $[\text{Cr}(\text{salprn})(\text{H}_2\text{O})_2]\text{Cl}$  reveals a less distorted coordination geometry around chromium when compared to a closer match of 12-membered analogue viz. *trans*- $[\text{Cr}(\text{salen})(\text{H}_2\text{O})_2]$ . The kinetics of the aqua ligand substitution in the complexes,  $\text{Cr}(\text{salprn})(\text{H}_2\text{O})_2^+$  and  $\text{Cr}(\text{salbuen})(\text{H}_2\text{O})_2^+$  by thiocyanate have been investigated under pseudo-first order conditions with  $[\text{NCS}^-] \gg [\text{Cr}(\text{III})]$  in the temperature range 10 to 50°C,  $[\text{H}^+] = 10^{-8} - 10^{-1} \text{ M}$  and  $l = 1.0 \text{ M}$  ( $\text{LiClO}_4$ ). The structure of the Schiff base with intraligand cavity sizes varying as 12, 13 and 14 influences the aqua ligand substitution rates significantly. The bimolecular rate constants for the various Schiff base complexes are  $1.5 \times 10^{-1}$ ,  $5.5 \times 10^{-4}$  and  $1.7 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  for salen, salprn and salbuen derivatives at 25°C respectively. The observed bimolecular rate constants will be discussed in terms of strain energy and ground state structural factors.

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