The Ligand Exchange Kinetics of a Five-co-ordinate Cobalt(II) Complex

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Summary The exchange kinetics of 2,6-lutidine *N*-oxide with Co(2,6-lutidine *N*-oxide)$_5{}^{2+}$ have been studied in CD_3NO_2–$(CD_3)_2CO$ (1 : 1 : v/v): the exchange rate was found to be independent of the free ligand concentration.

RECENTLY, the five-co-ordinate complexes of the bivalent first-row transition-metal ions have been much studied.[1] However, little is known about the solution behaviour of these complexes and no kinetic studies have been reported. We report here a study of the exchange reaction of Co(2,6-lutidine *N*-oxide)$_5{}^{2+}$ with an excess of 2,6-lutidine *N*-oxide.

The square-planar complex [Co(2,6-lutidine *N*-oxide)$_4$][ClO$_4$]$_2$ was first prepared by Karayannis *et al.*[2] and was found to assume a five-co-ordinate configuration in nitromethane in the presence of an excess of ligand. The structure of this five-co-ordinate 2,6-lutidine *N*-oxide complex is almost certainly trigonal bipyramidal based on the close similarity of its electronic spectrum to that of [Co(2-picoline *N*-oxide)$_5$][ClO$_4$]$_2$.[3] The latter complex has been shown to be trigonal bipyramidal in the solid state by an *X*-ray study[4] and has essentially the same electronic spectrum in solution as in the solid state.

We have shown that when [Co(2,6-lutidine *N*-oxide)$_4$][ClO$_4$]$_2$ is dissolved in CD_3NO_2–$(CD_3)_2CO$ (1 : 1) in the presence of an excess of ligand, a five-co-ordinate species of the type $CoL_5{}^{2+}$ is formed which is stable over a wide variety of conditions. Linear Beer's law plots passing through the origin were obtained at wavelengths of 565 and 850 nm for solutions containing 0·01M—0·08M-complex and ligand: complex concentration ratios varying from 6 : 1—50 : 1.

Kinetic studies of the exchange reaction

$$CoL_5{}^{2+} + L^* \rightleftharpoons [CoL_4L^*]^{2+} + L$$

where L represents 2,6-lutidine *N*-oxide, were carried out over the temperature range −50° to +40° using n.m.r. techniques. It was found that above *ca.* 5° fast exchange limiting conditions are present in the system. Below this temperature significant exchange broadening of the signal was observed.

Kinetic data were obtained from solutions containing free ligand concentrations of 4·47, 1·58, 1·07, and 0·67M and complex concentrations varying from 0·076—0·097M. Kinetic parameters were evaluated from the ligand 2,6-methyl signal using the equation[5]

$$\tau_m = \Delta\nu_{\frac{1}{2}}'/P_L^2 P_m 4\pi(\Delta\nu)^2$$

where τ_m represents the mean lifetime of a ligand in the primary co-ordination sphere, P_L and P_m are the mole fractions of ligand in the bulk solvent and the primary co-ordination sphere, respectively, $\Delta\nu$ is the isotropic shift, and $\Delta\nu_{\frac{1}{2}}'$ is the broadening of the signal at half height due to chemical exchange. This equation is applicable in the region near the fast exchange limit.[5] Values of $\Delta\nu$ and $\Delta\nu_{\frac{1}{2}}'$ in the exchange-controlled temperature region were obtained by extrapolation of the data from the fast exchange limiting region.

Values of τ_m were evaluated over the temperature range −5° to −25°. The exchange rate was found to be independent of the excess of ligand concentration and thus the exchange rate law is

$$\text{Rate} = \frac{5}{\tau_m}\,[\text{complex}].$$

The following kinetic parameters were obtained for Co(2,6-lutidine *N*-oxide)$_5{}^{2+}$: $1/\tau_m$ (25°) = $2{\cdot}0 \times 10^6\ s^{-1}$; $\Delta H^\ddagger$ 10·7 kcal mol^{-1}; and $\Delta S^\ddagger$ = 10 e.u.

Thus, these results show that this trigonal-bipyramidal complex exhibits a first-order exchange rate law which suggests that the exchange mechanism may be dissociatively controlled. The activation parameters also seem consistent with this mechanism.

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