"LIGAND EXCHANGE AND SUBSTITUTION IN FIVE-COORDINATE COMPLEXES OF COPPER(II), NICKEL(II) AND COBALT(II)"

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by

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CONTENTS

Summary (i)
Declaration (v)
Acknowledgements (vi)
CHAPTER 1 - INTRODUCTION 1
CHAPTER 2 - THE KINETIC AND EQUILIBRIUM METHODS EMPLOYED 18
CHAPTER 3 - EXPERIMENTAL DETAILS AND APPARATUS EMPLOYED 46
CHAPTER 4 - RESULTS 60
CHAPTER 5 - DISCUSSION 146
Appendices 181
Published papers from this work 208
A variety of five-coordinate transition metal complexes containing the triposa amino quadridentate ligand 2,2',2''-tri(4-dimethylamino)ethyamine of the form [M(Mo$_{4}$tren)$_{2}$]ClO$_{4}$; M = Co(II), Ni(II), Cu(II), Zn(II); S = dmf, def, dme, CH$_{3}$CN; have been prepared and characterized by elemental and metal analyses as well as by infrared spectroscopy.

These complexes were of interest as coordination of Mo$_{4}$tren ligand to divalent transition metal ions in this study produces a five-coordinate species in which solvent in the fifth coordination site exhibits a large reduction in lability compared to that exhibited by [M(solvent)]$^{2+}$. This is unusual as it has been reported widely in the literature that the labilities of six-coordinate Co(II) and Ni(II) species commonly exhibit significant increases in coordination of amine groups. It was hoped that this study would give some mechanistic insight into these unusually slowly reacting systems.

Complexes of the form [M(Mo$_{4}$tren)X]ClO$_{4}$ where M = Co(II), Ni(II), Cu(II); X = dmf, Br$^{-}$, N$_{3}^{-}$, NCS$^{-}$ were characterized in dmf solution by ultraviolet/visible absorption spectroscopy and the stoichiometry of mixed complexes was determined using the Job method of continuous variations.

Stopped-flow spectrophotometry at various temperatures has been used to examine the kinetics of amion reactions in dmf solution of [M(Mo$_{4}$tren)dmf]$^{2+}$; M = Co(II), Ni(II), Cu(II) with monodentate ligands: X$^{-}$ = Br$^{-}$, N$_{3}^{-}$, NCS$^{-}$ as shown below:

\[
[M(Mo$_{4}$tren)dmf]^{2+} + X^{-} \xrightarrow{k_{obs}} [M(Mo$_{4}$tren)X]^{+} + dmf
\]

The variation of $k_{obs}$ with excess $[X^{-}]$ for amion reactions on those complexes is consistent with the relationship:

\[
k_{obs} = k_{1}K_{0}[X^{-}]/(1 + K_{0}[X^{-}]) + k_{-1}
\]
which typifies an interchange (1) mechanism proceeding through two stages as shown below:

\[ [\text{M(Me}_{6}\text{tren})\text{dmf}]^{2+} + X^- \xrightarrow{k_0}{K_{\text{eq}}} [\text{M(Me}_{6}\text{tren})\text{dmf}]^{2+} \ldots X^- \]

\[ \frac{k_1}{k_{-1}} = [\text{M(Me}_{6}\text{tren})\text{X}]^{2+} + \text{dmf} \]

It has been found that there is little variation of \( k_1 \) with the nature of \( X^- \) for both the Ni(II) and Cu(II) complexes which suggests that the activation mode for the substitution of dmf by \( X^- \) is probably dissociative. However, for Co(II), there are marked differences in derived \( k_1 \) values on \( X^- \) is changed. This selectivity exhibited by \([\text{Co(Me}_{6}\text{tren})\text{dmf}]^{2+}\) towards substitution of dmf by \( X^- \) suggests that the activation mode is probably associative in this case.

Considering the above observations along with the observed ligand substitution rate laws it can be proposed that an associative interchange (\( \text{I}_{\alpha} \)) mechanism exists for anation on the Co(II) complex contrasting with the proposed dissociative interchange (\( \text{I}_{\alpha} \)) mechanism characterizing anation on both Ni(II) and Cu(II) complexes.

Proton nuclear magnetic resonance spectroscopy has been used to determine exchange rate and activation parameters for solvent exchange processes on \([\text{Co(Me}_{6}\text{tren})\text{S}]^{2+}\); \( S = \text{dmf}, \text{def}, \text{dmd} \) and \([\text{M(Me}_{6}\text{tren})\text{S}]^{2+}\); \( M = \text{Ni}(\text{II}), \text{Co}(\text{II}); S = \text{dmf}, \text{def} \) in solution in the following manner.

The variation of the relaxation parameter, \( T_{2\text{p}} \) was studied over a large temperature range (governed by solvent physical properties) for a number of solutions of each complex at differing concentrations. The form of \( T_{2\text{p}} \) for one solvent molecule at a single site is given according to Swift and Connick by the equation:

\[ \frac{1}{T_{2\text{p}}} = \frac{P_m}{2\text{p}} \left( \frac{T_{2\text{m}}^{-2}}{T_{2\text{m}}^{-1} + \Delta_{\text{m}}^{-2}} \right) + \frac{P_m}{2\text{p}} \left( \frac{T_{2\text{m}}^{-2}}{T_{2\text{m}}^{-1} + \Delta_{\text{m}}^{-2}} \right) \]
For each of the Cu(II) and Co(II) complexes studied the above equation over the temperature range considered reduces to

\[(Pn_{2g})^{-1} = r_n^{-1} = \left(\frac{k_B T}{h}\right)^0 e^{-\Delta H^*/RT} e^{\Delta S^*/R} + A_e e^{-E_e/RT}\]

where \(r_n\) is the mean lifetime of a coordinated solvent molecule and is related to the rate constant for solvent exchange, \(k_{ex}\), by the following relation

\[r_n^{-1} = k_{ex}\]

and the solvent, S, exchange rate is \(k_{ex} [N(MO_{6-tr})S^2] \) (\(M = Cu, Co\)).

The derivation of kinetic parameters for solvent exchange in the case of the Ni(II) complex was complicated by the presence of a minor species believed to be \([Ni(MO_{6-tr})S(df)_2]^2+\), but with some appropriate assumptions made, a similar approach to the Cu(II) systems was used to obtain kinetic parameters.

Volume of activation data from other variable pressure nmr studies have been obtained for each system and \(\Delta V^R\) for the Cu(II) systems was found to be positive, indicating a dissociative activation mode for solvent exchange on these complexes. \(\Delta V^R\) for solvent exchange on the Co(II) systems was also obtained and found to be negative, indicating an associatively activated mode for solvent exchange in these cases.

For the \(d^7\) Co(II) complex \([Co(MO_{6-tr})S(df)_2]^2+\) in dmf solution the significant dependence of \(k_1\) on the nature of incoming anion reacting through a proposed \(1_4\) mechanism seems to be consistent with a proposed associatively activated mechanism for dmf exchange already determined.

For the analogous \(d^8\) Ni(II) and \(d^9\) Cu(II) complexes in dmf solution the following may be deduced in each case. The similarity of \(k_{ex}\) to \(k_1\) and the small variation of \(k_1\) with differing entering anions suggest an \(1_4\) mechanism for ligand substitution on these complexes, consistent with the
proposed dissociatively activated mechanism for solvent exchange.

These new observations support the argument that ligand substitution in these complexes tends towards an associative activation mode as the electronic occupancy of the d orbitals on the central metal ion decreases. By comparison with other systems of distinct structure possible effects of stereochemistry on this tendency have also been discussed. Possible reasons for the unusually low lability of these complexes have also been discussed.