

that NH_3 and (I) are "normal" ligands,⁷⁻⁹ so the values of k_f , at least for the L_2M species which contain two or more replaceable *cis*-water molecules, may reasonably be compared; the k_d and K values for Co^{II} and Zn^{II} reflect the chelating nature of (I), however.

There is a remarkable similarity between the patterns for Co^{II} and Zn^{II} , and the contrast between these patterns and the one for Ni^{II} . The rate constants show a greater variation than the equilibrium constants for all three metals. As for Mg^{II} , Mn^{II} , and Ni^{II} , charge does not appear to be the dominant factor affecting the rates. It is also unlikely that crystal field effects are important for Co^{II} since they would be absent for Zn^{II} . It is possible that the relative

positions of the non-replaceable groups around the metal ion are important in these reactions with (I), and we have further evidence¹⁰ that the rearrangement of the non-replaceable groups necessary to accommodate the incoming bidentate ligand can considerably reduce k_f . Activation parameters are being measured for these and similar systems in the hope that they will reflect such factors.

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¹ E.g. M. E. Riepe and J. H. Wang, *J. Amer. Chem. Soc.*, **1967**, **89**, 4229; *J. Biol. Chem.*, **1968**, **243**, 2779.

² E.g. R. T. Simpson and B. L. Vallee, *Biochemistry*, **1968**, **7**, 4343.

³ E.g. B. L. Vallee, and R. J. P. Williams, *Proc. Nat. Acad. Sci. U.S.A.*, **1968**, **59**, 498.

⁴ D. N. Hague and M. Eigen, *Trans. Faraday Soc.*, **1966**, **62**, 1236.

⁵ D. N. Hague and M. S. Zetter, *Trans. Faraday Soc.*, **1970**, **66**, 1176.

⁶ D. W. Margerum and H. M. Rosen, *J. Amer. Chem. Soc.*, **1967**, **89**, 1088; J. P. Jones, E. J. Billo, and D. W. Margerum, *ibid.*, **1970**, **92**, 1875.

⁷ G. R. Cayley and D. N. Hague, *Trans. Faraday Soc.*, in the press.

⁸ E.g. M. Eigen and R. G. Wilkins, "Mechanisms of Inorganic Reactions," ed. R. F. Gould, Advances in Chemistry Series, No. 49, Amer. Chem. Soc., Washington, D.C., **1965**, p. 55; D. J. Hewkin and R. H. Prince, *Coordination Chem. Rev.*, **1970**, **5**, 45.

⁹ D. B. Rorabacher, *Inorg. Chem.*, **1966**, **5**, 1891.

¹⁰ M. A. Cobb and D. N. Hague, to be published.