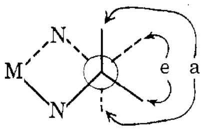
Chelate Ring Conformations and Substitution Rates of Cobalt(III) Complexes

Sir:

In Gillard and Irving's[1] excellent review on conformational aspects of chelate rings these authors briefly touch upon the relationship between aquation rates of *trans*-dichlorobis(diamine)cobalt(III) ions and chelate ring conformations present in these complexes. They simply noted that there was a parallel between expected instability of the chelate rings and the aquation rates. Their review reveals vividly how much has been said concerning the dependence of thermodynamic stability of complexes on chelate ring conformations and how little has been said about conformational effects on reaction kinetics and mechanism. The particular case touched upon by the reviewers, the aquation of *trans*-$[Co(diamine)Cl_2]^+$ ions, is worthy of more lengthy discussion.

According to Corey and Bailar's[2] chelate ring conformational analysis, positions on the carbon atoms of ethylenediamine chelate rings possess axial (a) or equatorial (e) character as shown below. Hence, for C-methyl-substituted ethylenediamine chelate rings, the methyl groups may occupy either axial or equatorial positions. In octahedral complexes equatorial positions are energetically preferred because of strong steric interactions between axial methyl groups and groups in octahedral coordination sites perpendicular to the chelate ring.[2,3]



In Table I are given rate data, obtained by Pearson, *et al.*,[4] for the aquation of *trans*-$[Co(diamine)_2Cl_2]^+$ ions in which the diamines are ethylenediamine and N- and C-alkylethylenediamines. Also, in this table are given the number of axial methyl groups predicted for each complex. Note the striking correlation between number of axial methyls and aquation rate constants. For all six complexes in which no axial methyl groups are expected, the aquation rates are all in the same order of magnitude ($k_1 = 1.0\text{–}8.8 \times 10^{-3}$ min^{-1}). The rates for the two complexes containing two axial methyl groups are within a factor of 2 of each other ($k_1 = 130\text{–}230 \times 10^{-3}$ min^{-1}) and more than 10 times faster than the fastest aquating complex containing no axial methyls. Finally, in the case of the complex containing four axial methyls, the aquation rate is essentially instantaneous.

TABLE I

RATES OF AQUATION OF *trans*-$[Co(AA)_2Cl_2]^+$

$$[Co(AA)_2Cl_2]^+ + H_2O \longrightarrow [Co(AA)_2OH_2Cl]^{2+} + Cl^-$$

AA	10^3k, min^{-1} [a]	No. of axial methyl groups
Ethylenediamine	1.9	0
N-Methylethylenediamine	1.0	0
N-Ethylethylenediamine	3.6	0
N-Propylethylenediamine	7.1	0
dl-Propylenediamine	3.7	0
dl-Butylenediamine	8.8	0
meso-Butylenediamine	250	2
Isobutylenediamine	130	2
Tetramethylethylenediamine	Instantaneous	4

[a] From R. G. Pearson, C. R. Boston, and F. Basolo, *J. Am. Chem. Soc.*, **75**, 3089 (1953); rates in aqueous solution at pH 1 and 25°.

Noting, as a general trend, that the rate of aquation of the compounds increases as the bulkiness of the diamines increases, Pearson, *et al.*,[4] postulated that the reactions proceed *via* an SN1 mechanism as opposed to an SN2. This conclusion in the case of *trans*-$[Co(en)_2Cl_2]^+$ has been substantiated by more recent work.[5]

The rate dependence on the number of axial methyls for the other compounds is consistent with the proposed SN1 mechanism. Axial methyls are predicted to interact sterically with the chloro groups. For an SN1 process lengthening of the chloride–cobalt(III) bond in the activated complex should relieve some of this interaction. This should result in a lowering of the activation energy and an increase in reactivity toward aquation. These kinetic data are seen, therefore, to provide excellent experimental evidence in support of Corey and Bailar's chelate ring conformational analysis.

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[1] R. D. Gillard and H. M. Irving, *Chem. Rev.*, **65**, 603 (1965).

[2] E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

[3] (a) F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *J. Am. Chem. Soc.*, **85**, 2913 (1963); (b) Y. Saito and H. Iwasaki, "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p 557.

[4] R. G. Pearson, C. R. Boston, and F. Basolo, *J. Am. Chem. Soc.*, **75**, 3089 (1953).

[5] (a) C. Ingold, R. S. Nyholm, and M. L. Tobe, *Nature*, **187**, 477 (1960); (b) M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961).