Hydrogen-Deuterium Exchange of Several Optically Active Complexes of Cobalt(III) in D_2O Solutions

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The rates of hydrogen isotope exchange were measured for several optically-active cationic cobalt complexes dissolved in D_2O containing an optically-active anionic species. The rate constant was obtained from the plot of $-\log(1-A_t/A_\infty)$ *vs.* t,[1] where A_t is the observed absorbance at 6000 cm^{-1} (due to HDO) at time t and where A_∞ is the equilibrium value. A Carl-Zeiss spectrophotometer PMQII was used for the measurements.

The rates of amino-hydrogen exchange for *d*- and *l*-$[Co(en)_3]^{3+}$ were measured in the presence of *d*-tartrate.[*1] The results are given in Table 1. The conditions were practically the same within each pair of runs, except that different optical isomers of the complex were used. In the pair of runs, D-0 and L-0, where the solution contained no tartrate, but instead an acetate buffer, the rates of hydrogen exchange were very similar. In the presence of *d*-tartrate, however, the rate constants were appreciably smaller for *d*-$[Co(en)_3]^{3+}$ than for the *l*-isomer. This seems to imply that there is some stereoselective interaction in the solution between the isomers of $[Co(en)_3]^{3+}$ and the *d*-tartrate ion. In this connection, it is interesting to note that Ogino and Saito obtained a higher association constant for the pair consisting of *d*-$[Co(en)_3]^{3+}$ and *d*-tartrate.[2]

TABLE 1. RATE CONSTANTS FOR THE HYDROGEN EXCHANGE OF *d*- AND *l*-$[Co(en)_3]^{3+}$ (25°C)

Sample No.	Complex $\times 10^2$M	*d*-tartrate $\times 10^2$M	pH**	k $\times 10^4$ sec^{-1}
D-0**	*d* 3.02	0.00	4.75	6.70
L-0**	*l* 3.00	0.00	4.75	6.69
D-1	*d* 3.28	3.06	4.77	4.70
L-1	1 3.21	3.13	4.81	5.24
D-2	*d* 3.07	3.10	4.79	4.82
L-2	*l* 3.02	3.10	4.79	5.04
D-3	*d* 2.93	5.11	5.38	15.1
L-3	*l* 2.90	5.11	5.38	17.0
D-4	*d* 2.94	6.95	5.21	8.47
L-4	*l* 2.90	6.95	5.21	10.9
D-5	*d* 2.92	9.93	5.37	9.61
L-5	*l* 2.90	9.93	5.37	10.8

* Values given are apparent pH values measured with a usual pH meter in D_2O solution.

** The run was carried out in an acetate buffer solution.

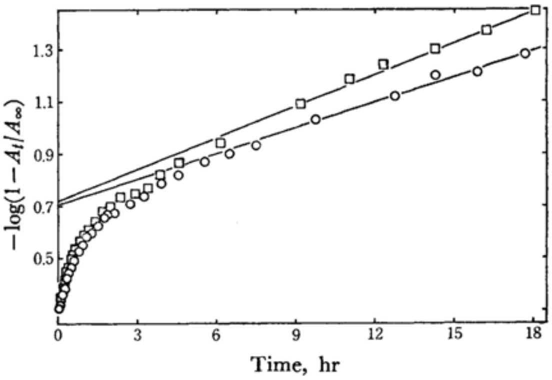

Fig. 1. Hydrogen exchange for *d*- (○) and *l*-$[Co(NO_2)_2(en)_2]^+$ (□) in the presence of *l*-$[Co(EDTA)]^-$.

TABLE 2. RATE CONSTANTS FOR THE HYDROGEN EXCHANGE OF *d*- AND *l*-$[Co(NO_2)_2(en)_2]^+$ (25°C)

Sample No.	Complex $\times 10^2$M	*l*-$[CoY]^-$ *** $\times 10^2$M	pH*	k $\times 10^5$ sec^{-1}
D-0**	*d* 3.90	0.00	6.29	12.0
L-0**	*l* 3.87	0.00	6.29	12.0
D-1	*d* 3.88	3.49	6.07	1.93
L-1	*l* 3.90	3.49	6.07	2.25

*, ** See corresponding reference in Table 1.

*** Y=EDTA

Similar results were obtained for *d*- and *l*-$[Co(NO_2)_2(en)_2]^+$ in the presence of *l*-$[Co(EDTA)]^-$, as is shown in Fig. 1 and Table 2. In this case, the amino groups are not equivalent and *at least* two exchange rates may be expected.[3] Table 2 gives data for the smallest rate constant, which is probably due to amino groups *cis* to nitro groups.

Further results and a more detailed discussion will be given elsewhere.

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[1] See, *e.g.*, H. A. C. McKay, *Nature*, **142**, 997 (1938).

[*1] The notations *d* and *l* in this communication mean, as usual, that the compound is dextrorotatory or levorotatory respectively at the sodium D line.

[2] K. Ogino and U. Saito, This Bulletin, **40**, 826 (1967).

[3] J. W. Palmer and F. Basolo, *J. Phys. Chem.*, **64**, 778 (1960).