Intramolecular Substitution Reactions of Binuclear Complexes of Cobalt

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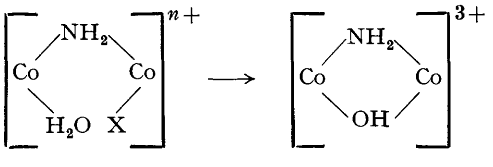
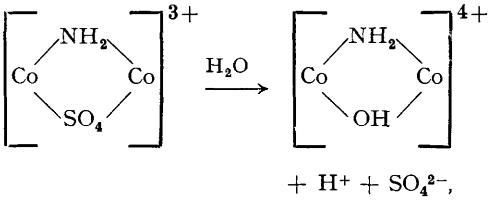
INTRAMOLECULAR substitution reactions of octamminedicobalt(III) complexes



(1)

where X = Cl^-, Br^-, NO_3^- and H_2O, and the reaction



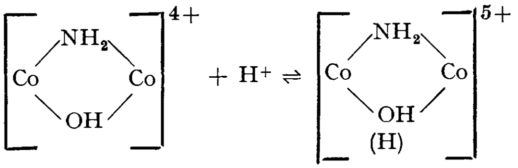
(2)

have been studied using conventional spectrophotometric techniques. Samples of the complexes $(NH_3)_4(H_2O)Co,NH_2,Co(Cl)(NH_3)_4^{4+}$, $(NH_3)_4$-$(H_2O)Co,NH_2,Co(Br)(NH_3)_4^{4+}$, $(NH_3)_4Co,\mu(NH_2,$-$SO_4),Co(NH_3)_4^{3+}$, and $(NH_3)_4Co,\mu(NH_2,OH),Co,$-$(NH_3)_4^{4+}$ were prepared by methods used by Werner.[1] Reaction solutions were of perchloric acid made up to ionic strength $\mu = 2{\cdot}0$M with sodium perchlorate.

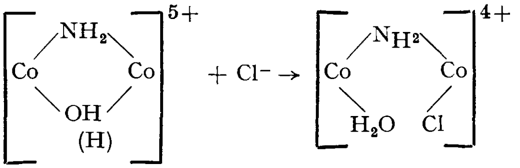
With the aquo-chloro-complex, (X = Cl^-), reaction (1) does not proceed to completion and both forward and back reactions are readily studied (as in chlorohydrin—epoxide conversions[2]). First-order rate constants *k* for the forward reaction show only a small dependence on ionic strength and hydrogen-ion concentration, the latter being attributed to medium effects. For the back reaction the rate equation is of the form

$$\text{Rate} = k'[\mu(NH_2, OH)][Cl^-][H^-],$$

which is consistent with a rapid protonation reaction



followed by the rate-determining step



With the other reactants the back reaction is much slower.

In the Table, rate constants for the forward reactions are shown alongside data for the acid hydrolysis of mononuclear pentamminecobalt(III) complexes

$$Co(NH_3)_5X^{n+} + H_2O \rightarrow Co(NH_3)_5H_2O^{3+} + X.$$

Rate constants for the intramolecular reactions are appreciably bigger than those for the reactions of the corresponding mononuclear complexes. From the data given it can be reasoned that conversion of the aquo-chloro-, aquo-bromo-, and

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[1] A. Werner, *Annalen*, 1910, **375**, 1.

[2] See, for example, A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms", J. Wiley, 1961, pp. 288–305.

aquo-nitrato-complexes to the $\mu(NH_2, OH)$ complex must proceed at least predominently by the direct path, and not with intermediate formation of the diaquo-form.

TABLE

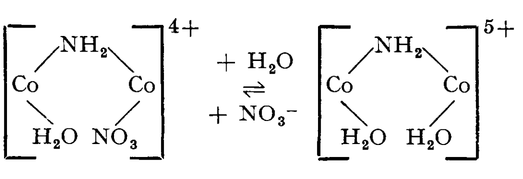
A comparison of data for substitution reactions of binuclear and mononuclear complexes

Binuclear complex	$k \times 10^5$ at 25° c (l. mole^{-1} sec.$^{-1}$)	E (kcal. mole^{-1})	$\log_{10}A$	Mononuclear Complex	$k \times 10^5$ at 25° c (l. mole^{-1} sec.$^{-1}$)	E (kcal. mole^{-1})	$\log_{10}A$
Aquo-chloro ..	8·28	19·2	9·91	$Co(NH_3)_5Cl^{2+}$	0·17[b]	24	11·73
Aquo-bromo ..	37·58	18·6	10·03	$Co(NH_3)_5Br^{2+}$	0·63[b]	24	12·3
Aquo-nitrato ..	65·0[a](1·7° c)	—	—	$Co(NH_3)_5NO_3^{2+}$	2·66[c]	26	4·39
Diaquo	6·46	19·9	10·36	$Co(NH_3)_5H_2O^{3+}$	0·66[d]	27	14·98
$\mu(NH_2,SO_4)$ ..	0·44	18·2	7·92	$Co(NH_3)_5SO_4^{+}$	0·12[e]	19	7·94

[a] Rate constants extrapolated to zero free nitrate. [b] A. W. Adamson and R. G. Wilkins, *J. Amer. Chem. Soc.*, 1954, **76**, 3379. [c] J. N. Brønsted, *Z. phys. Chem.*, 1926, **122**, 383. [d] A. C. Rutenberg and H. Taube, *J. Chem. Phys.*, 1952, **20**, 823. [e] H. Taube and F. A. Posey, *J. Amer. Chem. Soc.*, 1953, **75**, 1463.

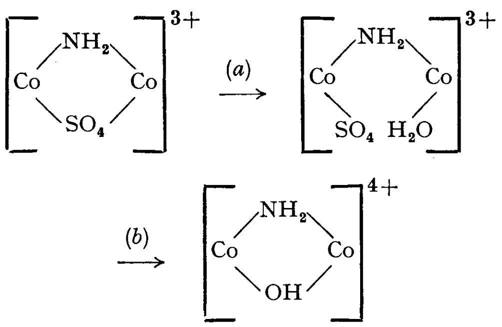
The diaquo-complex has not previously been prepared. Crystals which are obtained by treating the $\mu(NH_2, OH)$ complex with concentrated nitric acid and cooling to 0° c, and which we previously reported as being the nitrate salt of the aquo-nitrato-complex $(NH_3)_4(NO_3)Co,NH_2,Co(H_2O)(NH_3)_4^{4+}$,[3] we now believe to be the nitrate salt of the diaquo-complex $(NH_3)_4(H_2O)Co,NH_2,Co(H_2O)(NH_3)_4^{5+}$. Thus on conversion into the bromide salt the sample analysed correctly for the diaquo- and not the aquo-nitrato-form. The diaquo-complex was also prepared by treating the $\mu(NH_2, OH)$ complex with concentrated perchloric acid. Since spectra (260—600 mμ) and kinetic data are identical for both samples, formation of significant amounts of the aquo-perchlorato-complex is unlikely.

When nitric acid (*ca.* 10N) is added to the $\mu(NH_2, OH)$ complex spectral observations indicate that an equilibrium*



is set up. It is possible to study the conversion of the aquo-nitrato-complex into the $\mu(NH_2, OH)$ complex by diluting such solutions and recording optical density changes at the 528 mμ isosbestic point for the diaquo and $\mu(NH_2, OH)$ complex.

In reaction (2) the aquo-sulphato-complex is almost certainly formed as an intermediate, thus



It is not unreasonable that the second stage (*b*) of such a scheme is some twenty-five times faster than (*a*), and that (*a*) is therefore rate-determining. Attempts to isolate the aquo-sulphato-complex have so far proved unsuccessful.

Because activation energies in the Table are only moderately high, *cis*-attack[4] of the co-ordinated water molecule seems likely (*i.e.* the X and H_2O ligands in the binuclear complexes are in adjacent positions). That activation energies for the aquo-binuclear complexes are 6—7 kcal. mole^{-1} smaller than those for the mononuclear complexes is probably due to the reduced stability of the dicobalt complexes (which can in turn be attributed to steric effects).

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* We assume here that the aquo-nitrato- and not the $\mu(NH_2, NO_3)$ complex is formed.

[3] R. D. Mast and A. G. Sykes, *Chem. Comm.*, 1965, 270.

[4] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", J. Wiley, 1958, p. 100—101.