Interconversions of Binuclear Complexes of Cobalt

By K. GARBETT and R. D. GILLARD

(*Department of Chemistry, The University, Sheffield,* 10)

IN connection with our studies of chemical correlation of optical configurations, we have required detailed knowledge of the nature of the complex ions obtained in such reactions as the aquation of the cation $[en_2Co(\mu\mu\text{-}NH_2,SO_4)Coen_2]^{3+}$. While there is some information available on the interconversions of the optically inactive complexes with ammonia as ligand, little is known about the analogous complexes of ethylenediamine.

The reactions so far demonstrated are collected in the flow sheet. The nature of compounds A and B is well known.[1] The reaction of iodide ion

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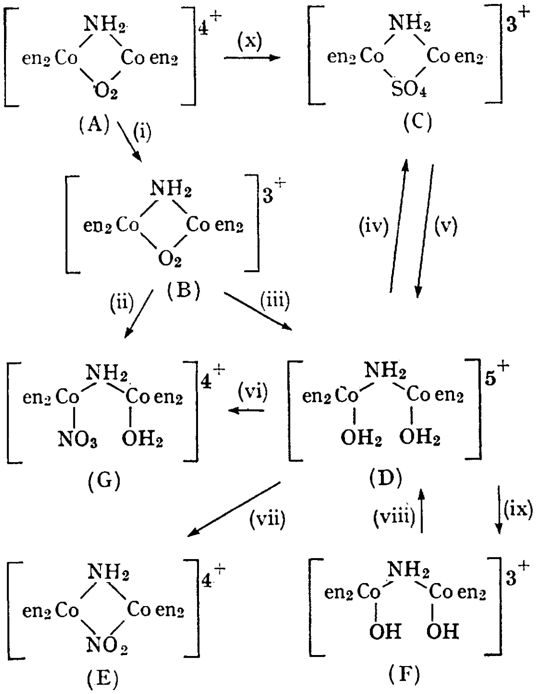
[1] L. R. Thompson and W. K. Wilmarth, *J. Phys. Chem.*, 1952, **56**, 5.

in acid solution with the complex of ammonia analogous to A shows a 3 : 1 stoicheiometry;[2] a 3 : 1 ratio is now also found for the conversion of A into D, with B as an intermediate formed by the reaction of the first equivalent of iodide ion.

D is obtained from B if acetic acid or dilute sulphuric acid is used. D is also produced by aquation of C. In the ammonia series, it was thought[2] that the reaction of the analogue of A (and hence of B) with iodide led to the formation of mononuclear complexes of cobalt (III). In fact, the amino-bridge in D is not easily broken.

That D is a binuclear species is shown by several observations. Solutions of resolved C, when set aside, slowly mutarotate[3] forming optically active D, whose rotation is steady. Also if mononuclear products were obtained, *cis*-bisaquobisethylenediaminecobalt(III) cation would be present, which, on treatment with base, would change,[4] at a measurable rate, into an equilibrium mixture of *cis* and *trans*-dihydroxobisethylenediaminecobalt-(III) salts. However, D (λ 500 mμ, ϵ 180) on treatment with base, immediately forms F (λ 477 mμ, ϵ 140) and no further change in spectrum is observed. Finally, D reacts with nitrite ion to form the known E, and with sulphuric acid to form C.

When nitric acid and iodide ion react with A, D is not obtained. Instead, G (λ 475, ϵ 210) is formed. G is also obtained by treating D with nitric acid. The original preparation[5] of [en$_2$ Co($\mu\mu$-NH$_2$,OH)Co en$_2$]$^{4+}$ from A utilized hydriodic acid made *in situ* with acetic acid. The product has a spectrum identical with that of D, so that it seems probable that the $\mu\mu$-amino-hydroxide complex exists as the bisaquo-complex, D, in aqueous solution. G therefore corresponds to Werner's nitrato-aquo-complex[6] with a single amino-bridge.



(i) I$^-$. (ii) 2I$^-$/HNO$_3$. (iii) 2I$^-$/2N-H$_2$SO$_4$. (iv) conc. H$_2$SO$_4$. (v) H$_2$O. (vi) HNO$_3$. (vii) H$^+$/NO$_2^-$. (viii) H$^+$. (ix) OH$^-$. (x) SO$_2$/H$_2$O.

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[2] A. G. Sykes, *Trans. Faraday Soc.*, 1963, **59**, 1343.
[3] J. P. Mathieu, *Bull. Soc. Chim. France*, 1938, **5**, 105.
[4] J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, 1952, **6**, 1265.
[5] A. Werner, *Ber.*, 1914, **47**, 1976.
[6] A. Werner, *Annalen*, 1910, **375**, 12.