Interconversion Reactions of Binuclear Complexes of Cobalt

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IN studying the solution reactions of binuclear (ammine) complexes of cobalt we have found a certain amount of disagreement with the recently reported results of Garbett and Gillard[1] (using ethylenediamine complexes). We give below details of our flow sheet for the reactions in question.

The 3 : 1 reaction of iodide with the peroxo-complex (A) results in the formation of (D), where (B) is no doubt formed as an intermediate by the reaction of the first equivalent of iodide. That the product (D) (λ_{max} 520 mμ, ϵ 151) is the double-bridged complex as shown and not a single-bridged bisaquo-complex of the type suggested by Garbett and Gillard, is readily demonstrated. Thus the chloride salt of the complex $(NH_3)_4Co,\mu(NH_2,OH),Co(NH_3)_4{}^{4+}$ can be prepared by the method used by Werner,[2] and this is found to have a spectrum identical with that of (D). Analysis for hydrogen and chlorine (H = 7%, Cl = 28·2%) confirms the formula $(NH_3)_4Co,\mu(NH_2,OH),Co(NH_3)_4Cl_4,4H_2O$ (H = 7%, Cl = 28·35%), and excludes the single-bridged bisaquo-structure $(NH_3)_4(H_2O)Co,NH_2,Co(H_2O)(NH_3)_4Cl_5,4H_2O$ (Cl = 32%). It is unlikely that the double-bridged complex is rapidly converted into the bisaquo single-bridged complex in solution owing to the chemical inertness of cobalt(III) ions. Furthermore, in our reactions of Cr^{2+} with binuclear complexes of cobalt,[3] (C) and the chloro-analogue of the nitrato-complex (G) react rapidly with Cr^{2+} (compare the reactions of $Co^{III}(NH_3)_5X^{n+}$ complexes with Cr^{2+}),[4] whereas (D) ($9·5 \times 10^{-3}$ l.mole^{-1}sec.$^{-1}$ in 1·0N-perchloric acid at 20°) and $(NH_3)_5Co.NH_2.Co(NH_3)_5{}^{5+}$ ($1·7 \times 10^{-3}$ l.mole^{-1} sec.$^{-1}$ at 20°) react much slower (compare the reaction of $Co(NH_3)_6{}^{3+}$ with Cr^{2+}). In reactions of the first type inner-sphere transition complexes

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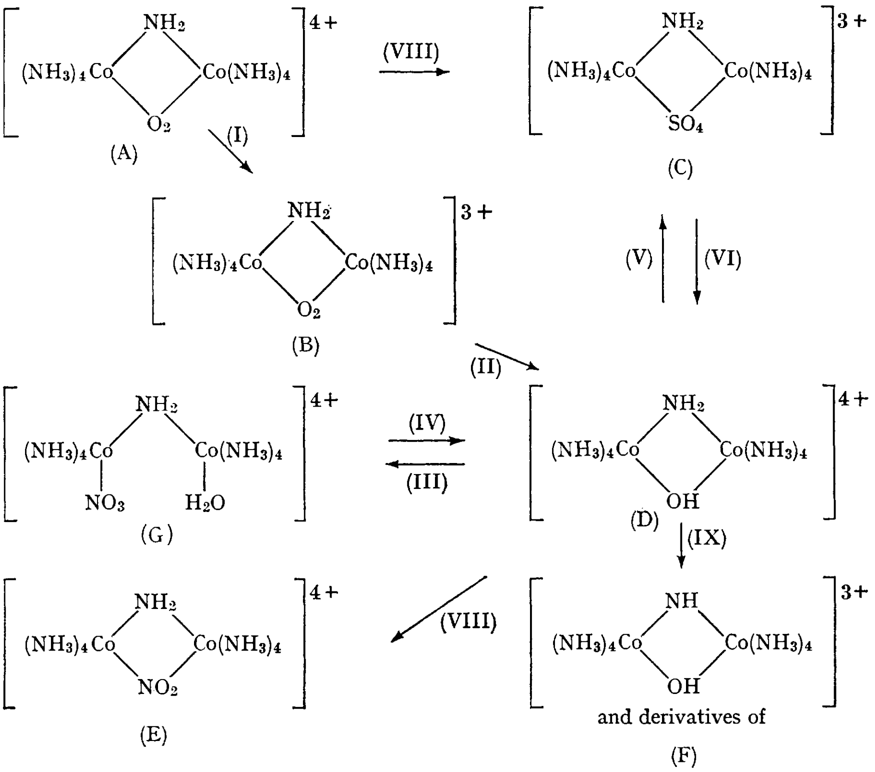
[1] K. Garbett and R. D. Gillard, *Chem. Comm.*, 1965, 45.

[2] A. Werner, *Ber*, 1907, **40**, 4605.

[3] R. D. Mast and A. G. Sykes, to be published.

[4] H. Taube and H. Myers, *J. Amer. Chem. Soc.*, 1954, **76**, 2103.

are formed, but in reactions of the second type transition complexes are almost certainly of the outer-sphere type. If (D) was a mono-bridged bisaquo-complex we would expect it to react at a much faster rate. Similar reasoning applies in the case of the ethylenediamine complexes. Thus the ethylenediamine analogue of (A) reacts with iodide to give a complex with spectrum identical to that of $(en)_2Co,\mu(NH_2,OH),Co(en)_2^{4+}$. It is unlikely that the latter (Werner's analysis, reference 5) is readily converted into a bisaquo-complex in solution, as is implied by Garbett and Gillard, again because cobalt(III) complexes are inert to substitution.



(I) and (II) I^-–dil. H^+. (III) conc. HNO_3. (IV) H_2O–$HClO_4$.
(V) 7M-H_2SO_4. (VI) H_2O–$HClO_4$. (VII) SO_3^{2-}.
(VIII) excess of NO_2^- (90°). (IX) NaOH–NH_4.OH.

On treating (D) with concentrated nitric acid the nitrato-complex (G) is formed almost instantly. Crystals of the nitrate salt were obtained by cooling to 0°, and a 0·001M solution in aqueous perchloric acid (λ_{max} 555 mμ, ϵ 168) reverted to (D) within one hour at 40°. With 7M-sulphuric acid, (D) readily formed the sulphato-complex (C) (λ_{max} 540 mμ, ϵ 344), and the same sulphato-complex is the principal product (~85%) from the reaction of sodium sulphite with (A) in 0·01N-acid (3 : 2 stoicheiometry). Hydrolysis back to (D) in sulphate-free solutions is in this case a much slower process. Conversion of (D) to the nitro-complex (E) (λ_{max} 481 mμ, ϵ 254) requires an excess of sodium nitrite and temperatures of around 90°. There is no detectable hydrolysis of (E) back to (D) over 7 hours at 40°.

Solutions of (A), (C), and (D) react with 0·1M-sodium hydroxide to give intense brown solutions which have spectra similar to that reported by Mathieu[6] for the imido-complex $(en)_2Co,\mu(NH,O_2).Co(en)_2^{3+}$ (*i.e.* the absorption steadily increases in

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[5] A. Werner, *Annalen*, 1910, **375**, 76.

[6] J. P. Mathieu, *Bull. Soc. chim. France*, 1938, **5**, 105.

going from 600 to 400 mμ and there is no maximum in this region). Although formation of imido-complexes seems likely the nature of these reactions is uncertain, and hydrolysis of other ligand groups is possible. The reactions are *not* in fact reversible and on acidifying mononuclear derivatives are eventually obtained. With ammonium hydroxide conversion of (D) is much less extensive, and again the reaction is not reversible with acid.

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