

Optical Configurations of Binuclear Complexes of Cobalt(III)

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THE well known binuclear complexes of cobalt(III) containing ethylenediamine may exist in enantiomeric forms. (There is also an optically inactive *meso*-isomer). The configurational label D in Figure 1 is based on the nomenclature¹ for the monomeric series containing the *cis*-bisethylenediamine moiety.

Mathieu² concluded from his spectroscopic

studies that the configurations of the binuclear complexes showed no direct relationship with the signs of the Cotton effects in the visible region, although certain binuclear complexes were related by chemical transformations.

We report the first correlation of the optical configurations of these binuclear complexes with those of the monomeric *cis*-bisethylenediamine

complexes. When the complex (+)-[en₂Co(NH₃)-μ(NH₂)(NH₃)Coen₂]⁵⁺ is allowed to react with a 1:1 mixture of sulphuric and hydrochloric acids for half an hour, the amino-bridge is broken on one side only, as shown in Figure 2.

There is no bond-breakage between cobalt and ligands in the formation of (B) from (A), so that (A) and (B) have related configurations. Since, in a resolved binuclear complex, both cobalt atoms of course have the same configuration, (B) and (C) also have related configurations. (-)-B is known from our earlier work¹ to have the

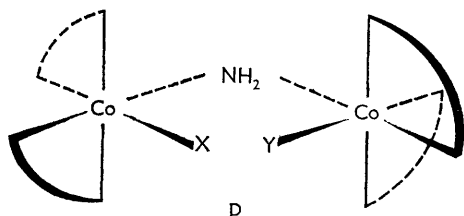


FIGURE 1. The D-enantiomer of binuclear complexes

L-configuration, so that (+)-A has the L-configuration (enantiomer of Figure 1.) Under the conditions of the reaction, (-)-B is transformed to (-)-C after a few hours, and (C) itself is very slowly converted into the *trans*-dichloro-complex.

(+)-A is derived from the less soluble diastereoisomer³ (-)-[en₂Co μμ' (NH₂,O₂)Coen₂] [(+)-BCS]₄·9H₂O. This, and the many other binuclear complexes obtainable from it (some typical compounds are in Figure 3) all have the L-configuration.

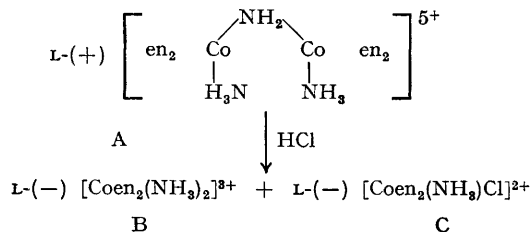


FIGURE 2. Conversion of binuclear into mononuclear complexes

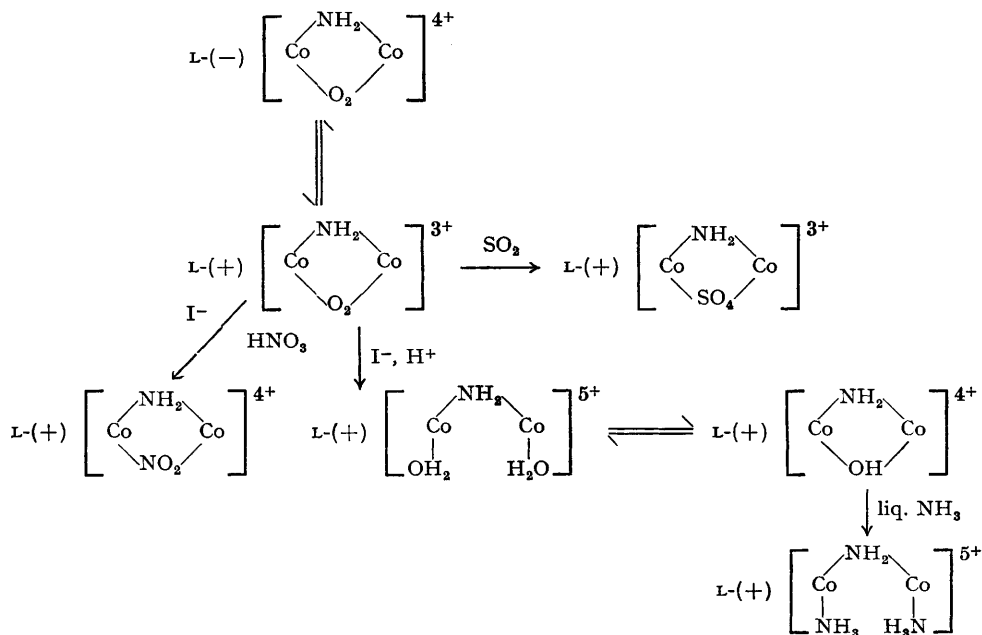


FIGURE 3. Interconversions of binuclear complexes of the L-configuration (the ethylenediamine ligands are omitted)

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¹ K. Garbett and R. D. Gillard, *J. Chem. Soc.*, 1965, 6084.

² J. P. Mathieu, *Bull. Soc. chim. France*, 1938, 5, 105.

³ A. Werner, *Ber.*, 1914, 47, 1961.