

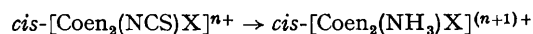
A Chemical Correlation of Optical Configurations in Werner Complexes

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FOR some co-ordination compounds containing polyatomic ligands, chemical reactions are known in which the metal-ligand bond is not broken. Thus, the cobalt-oxygen bond remains intact¹ when aquopenta-amminecobalt(III) ion forms from carbonatopenta-amminecobalt(III) ion in acid solution. Reactions of this kind are also possible with co-ordinated isothiocyanate groups; in acidic solutions, oxidation of $[\text{CoL}_5(\text{NCS})]^{n+}$ gave reasonable yields² of $[\text{CoL}_5(\text{NH}_3)]^{(n+1)+}$. Investigation³ of the kinetics of reactions of $[\text{Co}(\text{NH}_3)_5(\text{NCS})]^{2+}$ with various oxidants to form $[\text{Co}(\text{NH}_3)_6]^{3+}$ showed that only in the case of iodate as oxidant was there little or no formation of cobalt(II) ions during the reaction. Cobalt(II), of course, acts as a catalyst for the racemisation of optically active complexes of cobalt(III).

We have evaluated the use of acid iodate solutions as oxidants in the reactions



where X is Cl or H₂O. The reactions occurred with quantitative conversion into the ammine product. Since this product is thermodynamically unstable in acid solution, the Co-N bond remains intact throughout the reaction. This proves that the original complexes contained isothiocyanate ligands, bonded through nitrogen rather than sulphur.

Further, the conversions of A into B, and C into D, by iodate oxidation, have been achieved, correlating the optical configuration of A with that of B, and that of C with that of D.

The aquations⁴ of (+)₅₄₆₁-A to (+)₅₄₆₁-C, and of

¹ J. P. Hunt, A. C. Rutenberg, and H. Taube, *J. Amer. Chem. Soc.*, 1952, **74**, 268.

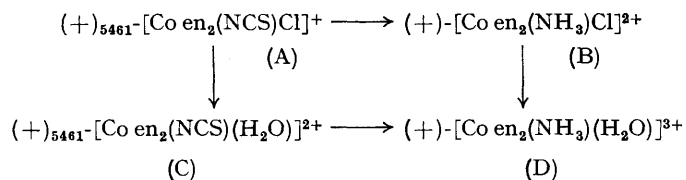
² A. Werner, *Z. anorg. Chem.*, 1900, **22**, 91; *Annalen*, 1912, **386**, 1; *Ber.*, 1911, **44**, 876.

³ K. Schug and M. D. Gilmore, Proc. 7th Internat. Conf. Co-ordination Chem., Stockholm, 1962, 274.

⁴ J. P. Mathieu, *Bull. Soc. Chim. France*, 1937, **4**, 687.

(+)-B to (+)-D have also been confirmed, though nothing can be said about relative optical configurations in these pairs.

longer wavelength and a positive Cotton effect at shorter wavelength, whereas (+)-B, which we have proved to have the same optical configuration



It so happens that the optical rotatory dispersion curves of A, B, C, and D in the region of the longest wavelength $d-d$ absorption band are all dominated by positive Cotton effects. However, the circular dichroism results⁵ in this region show that (+)₅₄₆₁-A has a negative Cotton effect at

as (+)₅₄₆₁-A, shows two positive Cotton effects. It is therefore apparent that configurational relationships for complexes cannot be derived from rotatory dispersion measurements alone.

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⁵ J. P. Mathieu, *Bull. Soc. chim. France*, 1936, **3**, 476.