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 intact[1] 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 $[CoL_5(NCS)]^{n+}$ gave reasonable yields[2] of $[CoL_5(NH_3)]^{(n+1)+}$. Investigation[3] of the kinetics of reactions of $[Co(NH_3)_5(NCS)]^{2+}$ with various oxidants to form $[Co(NH_3)_6]^{3+}$ 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

$$cis\text{-}[Coen_2(NCS)X]^{n+} \rightarrow cis\text{-}[Coen_2(NH_3)X]^{(n+1)+}$$

where X is Cl or H_2O. 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 aquations[4] of $(+)_{5461}$-A to $(+)_{5461}$-C, and of

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[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.

$$\begin{tikzcd}
(+)_{5461}\text{-}[\mathrm{Co\,en_2(NCS)Cl}]^{+} \arrow[r] \arrow[d, "\text{(A)}"] & (+)\text{-}[\mathrm{Co\,en_2(NH_3)Cl}]^{2+} \arrow[d, "\text{(B)}"] \\
(+)_{5461}\text{-}[\mathrm{Co\,en_2(NCS)(H_2O)}]^{2+} \arrow[r] & (+)\text{-}[\mathrm{Co\,en_2(NH_3)(H_2O)}]^{3+} \\
\text{(C)} & \text{(D)}
\end{tikzcd}$$

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 results[5] in this region show that $(+)_{5461}$-A has a negative Cotton effect at longer wavelength and a positive Cotton effect at shorter wavelength, whereas $(+)$-B, which we have proved to have the same optical configuration 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.