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OPTICAL CONFIGURATION OF WERNER COMPLEXES OF DIAMINES

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The biological importance of transition metal ions is becoming clear. One active field concerns the stereoselective effects usually observed in the interactions of optically active complex compounds with natural systems. One such stereoselective effect was recently discovered[1] in this laboratory for the non-heme iron protein, ferredoxin, which is involved in photosynthesis and in nitrogen fixation by anaerobic bacteria such as *Clostridium pasteurianum*. The iron atoms of natural ferredoxin do not exchange with radiolabelled iron in aqueous media; however, the iron may be rendered accessible to exchange (or to complexing by bipyridyl) in two ways, either by reduction (enzymically with hydrogen, or chemically, with dithionite) or by treatment with urea (which has the effect of denaturing many proteins through fission of hydrogen bonds). Tris(bipyridyl)iron(II) formed instantaneously from reduced ferredoxin is optically inactive, but that formed much more slowly from ferredoxin treated with urea is almost optically pure $(-)[\mathrm{Febipy_3}]^{2+}$. If the optical configuration of this complex were known, the helicity of the environment of the iron in ferredoxin could be deduced. In this, and many similar systems, a knowledge of the absolute configuration of complex compounds is required. Our studies on the relative and absolute configurations of diamine complexes are described here.

From the Bijvoet method of anomalous diffraction of X-rays, it is known[2] that the absolute configuration of the ion $(+)[\mathrm{Coen_3}]^{3+}$ is as shown in Fig. 1a.

Fig. 1. (a) The D or $S(C_3)R(C_2)$ configuration; ${}^1A_1 \rightarrow {}^1E_a$ along C_3 gives positive Cotton effect. (b) The D or $R(C_2)$ configuration for bischelate complexes. The transition along C_2 gives positive Cotton effect. (c) The effect of mercuric ion on the transition parallel to C_2 in $(+)[\mathrm{Coen_2(NCS)_2}]^{+}$.

This configuration may conveniently[3] be called D; a more fundamental notation[4,5] relies on the symmetry properties of the complex. It has a threefold axis (C_3) perpendicular to the plane of the paper and passing through the cobalt atom. On rotating the molecule clockwise about this axis, it behaves as a left-handed, or sinistral, propeller; this is denoted as $S(C)_3$, or in Piper's notation[6], Λ. The two fold axes (C_2) bisect the chelate rings, and helicity about these axes is right handed [$R(C_2)$]. The full description of the configuration is thus $S(C_3)R(C_2)$.

Optical configurations have recently been deduced in two ways. First, a large number of configurations have been determined[3,4,5] using stereoselective induction of configuration by optically active diamines, leading to such reference compounds as D(−)[Rhen$_3$]$^{3+}$, D(+)[Coen$_2$(Cl$_2$)]$^+$, and D(+)[Coen$_2$(NO$_2$)$_2$]$^+$. Secondly, for trischelate compounds with D_3 symmetry, spectroscopic studies based on ligand field theory have had a good deal of success, though there is at present some doubt[7] as to the interpretation of the results from absorption of polarized light by oriented single crystals. Until now, there has been no serious attempt to establish relative configurations of complex compounds by chemical means. For chemical correlations to be completely rigorous, there should be no fission of metal to ligand bonds during the relevant reaction. A number of cases of this type are discussed in this paper. For reaction of optically active complexes where metal to ligand bond breakage occurs, it is usually assumed that retention of configuration is the rule. This is proved for the acid catalysed aquation of nitro groups in such complexes as (+) [Coen$_2$(NO$_2$)$_2$]$^+$, and for the aquation of halo complexes of the type (+) [Coen$_2$XCl]$^{n+}$.

For the series of complexes *cis* [Coen$_2$XY]$^{n+}$, two methods have previously been applied[8] to establish rules connecting the optical rotatory properties of the complex with its absolute configuration. The first method involves comparisons of signs of Cotton effects, in rotatory dispersion or circular dichroism; a new rule is proposed here. The second method is that of less soluble diastereoisomers, which we use only to relate configuration of complexes containing cobalt with those of other metals.

CHEMICAL CORRELATIONS; REACTION WITH NO METAL–LIGAND BOND BREAKAGE

Isothiocyanate oxidation: Werner discovered[9] that complexes of the type [L$_5$Co(NCS)]$^{n+}$ could be oxidized in fair yield by chlorine or hydrogen peroxide, to [L$_5$Co(NH$_3$)]$^{(n+1)+}$. We have used acid iodate[10] as oxidant, and find that 100% conversion to the ammine complex occurs. The optically active complexes whose configurations have been related in this way are collected in Table I. Signs of rotation refer to the sodium yellow line unless otherwise stated.

The D configuration of (+) [Coen$_2$(NCS)$_2$]$^+$ is established spectroscopically as follows. It is known[7] for trischelate complexes like that in Fig. 1a, that the transition $^1A_1 \rightarrow {}^1E_a$ is parallel to the two fold axis, and gives a positive Cotton effect for the absolute configuration shown. On lowering the symmetry to C_2, the transition parallel to the two fold axis is now $^1A \rightarrow {}^1A$, which will still show a

TABLE I

ISOTHIOCYANATO → AMMINE CONVERSIONS

Factor[a]	*C.E.*[b]	*Product*[a]	*C.E.*
$(+)_{5461}[(NCS)Cl]^+$	[c]	$(+)[(NH_3)Cl]^{2+}$	[c]
$(+)[(NCS)(H_2O)]^{2+}$	+	$(+)[(NH_3)(H_2O)]^{3+}$	+
$(+)[(NCS)(NO_2)]^+$	+	$(+)[(NH_3)(NO_2)]^{2+}$	+
$(+)[(NCS)_2]^+$	+	$(+)[(NH_3)_2]^{3+}$	+
$(+)[(NCS)(NH_3)]^{2+}$	+	$(+)[(NH_3)_2]^{3+}$	+

[a] In the formulae for these complexes of the type $[Coen_2XY]^{n+}$, only the sign of rotation and X and Y are given. [b] The sign given is that for the longest wavelength Cotton effect. [c] Ambiguous, through overlapping of separate Cotton effects.

positive Cotton effect for the configuration of Fig. 1b. When the 1:1 adduct[11] with mercuric ion shown in Fig. 1c is formed, the transition parallel to the two fold axis will be most strongly affected. The positive Cotton effect at 490 mμ for (+) $[Coen_2(NCS)_2]^+$ shifts markedly on formation of the adduct. (+) $[Coen_2(NCS)_2]^+$ therefore bas the D configuration shown in Fig. 1b.

The product of oxidising this complex (see Table I) is (+) $[Coen_2(NH_3)_2]^{3+}$ which therefore also has the D configuration, $[R(C_2)]$, related to that of D(+) $[Coen_3]^{3+}$. The rotatory dispersion spectra of these enantiomers are given in Fig. 2. Despite the difference in molecular point groups, the configurations of the complexes may be compared using Cotton effects.

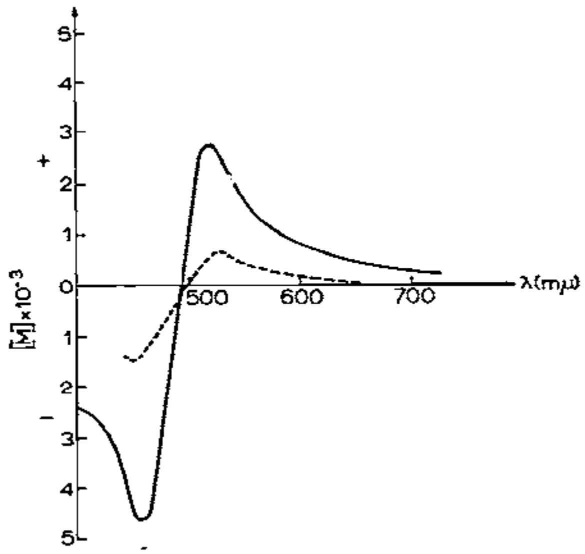

Fig. 2. The optical rotatory dispersion spectra of D(+) $[Coen_3]^{3+}$ (————) and D(+) $[Coen_2(NH_3)_2]^{3+}$ (– – – – –).

Aquo–nitro conversions: Aquo complexes of cobalt(III) react[12] with nitrite ion at pH 4 in the cold, forming nitrito complexes, without cobalt–oxygen bond breakage. The nitrito complex then isomerises[13] via an intramolecular mechanism to the corresponding N-bonded nitro complex, so that in the reactions:

$$\begin{tikzcd}
(+)\,[\mathrm{Coen_2X(H_2O)}]^{n+} \arrow[r] & (+)\,[\mathrm{Coen_2X(ONO)}]^{(n-1)+} \arrow[dl] \\
(+)\,[\mathrm{Coen_2X(NO_2)}]^{(n-1)+} &
\end{tikzcd}$$

optical configuration is retained. The reaction has been observed for $X = H_2O$, ONO, NO_2, NCS, Cl and NH_3.

When (+) $[\mathrm{Coen_2(NO_2)_2}]^+$ is treated with concentrated acid a catalysed aquation[14] occurs forming (+) $[\mathrm{Coen_2(NO_2)(H_2O)}]^{2+}$. Using the chemical correlations given above this reaction is seen to occur with retention of configuration. The similar replacements of nitro groups by water have been observed for (+) $[\mathrm{Coen_2X(NO_2)}]^{n+}$, where $X = NH_3$ and NCS. Again, configuration is retained.

Using results from the above reactions, and from the very simple aquo–hydroxo interconversions, the rule is proposed that, "For complexes of the type $[\mathrm{Coen_2XY}]^{n+}$, where X and Y are not halide ions, the complex has the D configuration if the longest wavelength Cotton effect in rotatory dispersion is positive."

Configuration of halo complexes

Spectroscopic splittings in halo complexes of the type $[\mathrm{Coen_2XCl}]^{n+}$ are rather large because of the weak ligand field of the halide ion compared with that of ½ en. For this reason, the rotatory dispersion spectra are often complex, and the simple rule above cannot be applied. *cis* Halo-complexes aquate with retention of geometrical configuration and it is usually assumed that optical configuration is retained also. This we have proved. First it may be shown that all aquo complexes aquate through a common optical mechanism (*i.e.* if inversion occurs in one such aquation it must occur in all.) One proof uses the conversions.

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

A and *B* are interconvertible and so have the same configuration; similarly, *C* and *D* are interconvertible. The two aquations shown by broken lines therefore occur with the same optical mechanism. Other similar proofs are possible.

The common optical mechanism involves retention, not inversion. This is proved by the following argument. The second aquation, that of *B* to *D*, occurs through the isorotatory points shown in Fig. 3. The observation of such points proves one of the following possibilities

(1) $100\ \mathrm{D}A \longrightarrow 100\ \mathrm{D}B$ (retention)
(2) $100\ \mathrm{D}A \xrightarrow{\frown} 100\ \mathrm{L}B$ (inversion)
(3) $100\ \mathrm{D}A \longrightarrow x\mathrm{D}B + (100-x)\ \mathrm{L}B$ (partial racemisation when $x \neq 50$; racemisation when $x = 50$, when the isorotatory points must coincide with the points at which the rotatory dispersion curve of DA crosses the axis of zero rotation).
(4) $100\ \mathrm{D}A \rightarrow x\ \mathrm{D}B + (100-x)C$ (where C is an inactive product; this would represent partial isomerisation).
(5) $100\ \mathrm{D}A \rightarrow x\ \mathrm{L}B + (100-x)C$
(6) $100\ \mathrm{D}A \rightarrow x\ \mathrm{D}B + y\ \mathrm{L}B + \{100-(x+y)\}C$

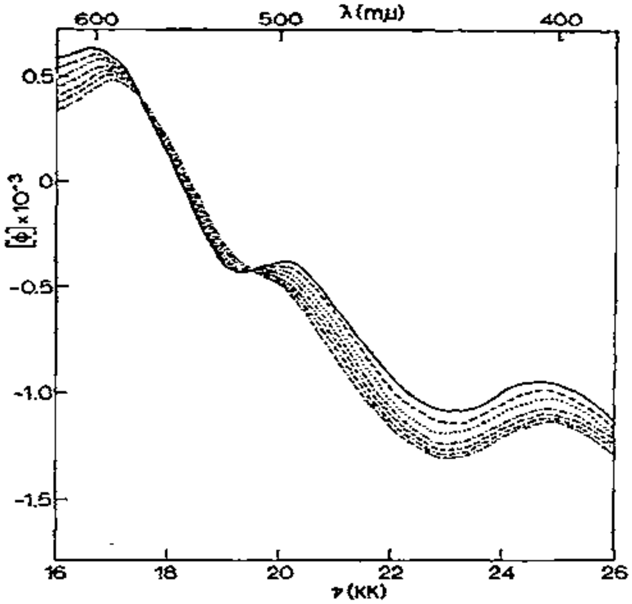

Fig. 3. Optical rotatory dispersion spectra during the aquation of (+) $[\mathrm{Coen_2(NH_3)Cl}]^{2+}$.

It is well established that aquations of *cis* halo complexes give *cis* aquo products, so cases (4), (5) and (6) may be ruled out. Case (3) is ruled out by the reactions.

$$(+)\ [(\mathrm{NO_2})\mathrm{Cl}]^+ \rightarrow \mathrm{D}(+)\ [(\mathrm{NO_2})\,(\mathrm{H_2O})]^{2+} \rightarrow \mathrm{D}(+)\ [(\mathrm{NO_2})_2]^+$$

The D(+) dinitro complex produced is optically pure, so that the nitro–aquo complex is optically pure, corresponding to case (1) or (2).

Case (2) (complete inversion) is usually excluded since if any inversion occurred, isomerisation should also occur. These mechanistic grounds are not quite rigorous, as shown in Fig. 4. For complete inversion (Fig. 4a) to occur, N_A and N_B must be very different in reactivity. Such differences are known among complexes of the garland amines, where N_A is terminal and free to move but N_B is non terminal and fixed; the conversion of triethylenetetramine complexes from the α to the β series (Fig. 4c) corresponds to inversion.

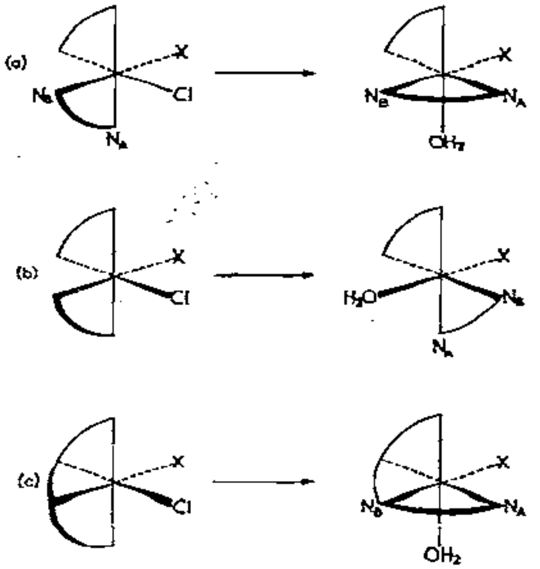

Fig. 4. Inversion and isomerisation as edge shifts. (a) Inversion. (b) Isomerisation. (c) Conversion of α-[Cotrien X Cl]$^{n+}$ to β-[Cotrien X(H$_2$O)]$^{(n+1)+}$ as a prototype inversion.

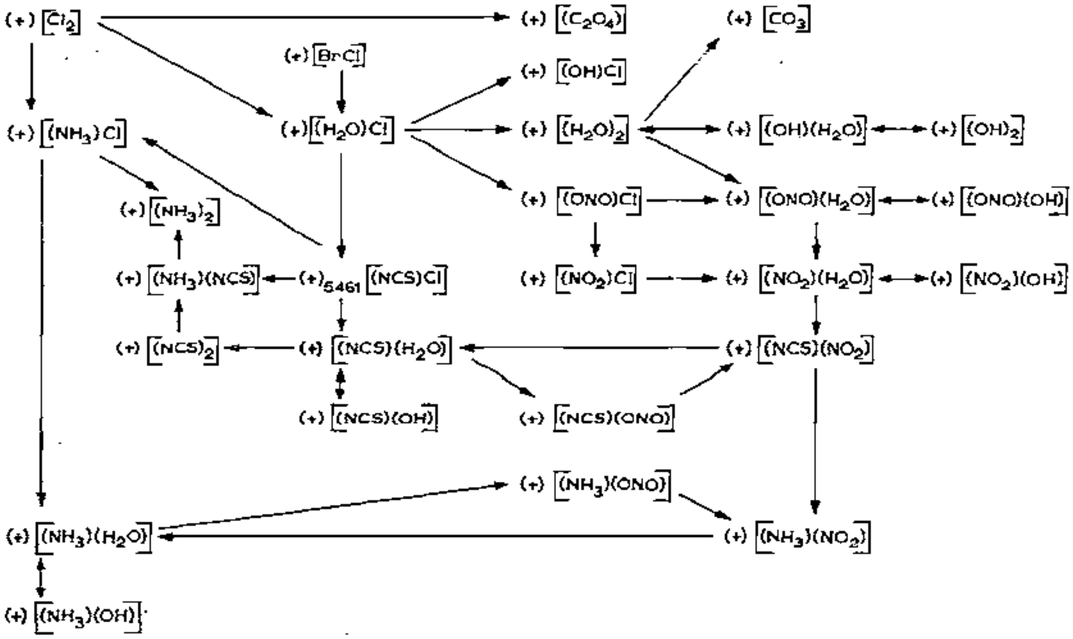

Fig. 5. Interconversions of optically active complexes of the series [Coen$_2$XY]$^{n+}$; all the complexes given have the D configuration.

In [$Coen_2XCl$], N_A is *trans* to NH_2 of ethylenediamine, whereas N_B is *trans* to X. When $X = NH_3$ the specific *trans* effect on N_A as against N_B required to give rise to complete inversion cannot exist. The reaction

$$(+)\,[Coen_2(NH_3)Cl]^{2+} \rightarrow (+)\,[Coen_2(NH_3)\,(H_2O)]^{3+}$$

shows isorotatory points (Fig. 3), so that this must correspond to case (1), retention of optical configuration.

Configurations of complexes of metals other than cobalt(III)

A grossly unreliable method (see Table II) which has often been used to compare configurations within the series $[Coen_2XY]^{n+}$ is that of less soluble diastereoisomers; we have restated this method in a rigorous form as follows. "If two enantiomers form isomorphous less soluble diastereoisomers with the same resolving agent, then they have related configurations". In this new form, the method is useful for comparing configurations of the analogous complexes of cobalt(III) and

TABLE II

RESOLUTIONS AND CONFIGURATIONS OF $[Men_2XY]^{n+}$

Complex	*(+)BCS*[a]	*(+)CS*[b]	*(+)SbOT*[c]	*D*[d]
$[Coen_3]^{3+}$	0[e]	0	(+)[f]	(+)
$[Coen_2Cl_2]^+$	(+)	(−)	(+)	(+)
$[Coen_2BrCl]^+$	(+)	(−)	(+)	(+)
$[Coen_2Br_2]^+$	(+)	0	(+)	(+)
$[Coen_2(N_3)_2]^+$	0	0	(+)	
$[Coen_2(CN)_2]^+$	(+)	0	0	
$[Coen_2(NO_2)_2]^+$	(+)	(−)	(−)	(+)
$[Coen_2(NCS)_2]^+$	(−)	0	(−)	(+)
$[Coen_2(NH_3)_2]^{3+}$	0	0	(+)	(+)
$[Coen_2(NH_3)Cl]^{2+}$	(+)	(−)	(−)	(+)
$[Coen_2(NH_3)Br]^{2+}$	(+)	0	(−)	(+)
$[Coen_2(NH_3)\,(NCS)]^{2+}$	(+)	0	0	(+)
$[Coen_2(NH_3)\,(NO_2)]^{2+}$	(−)	0	(−)	(+)
$[Coen_2(NO_2)\,(NCS)]^+$	(−)	0	(−)	(+)
$[Coen_2(NO_2)\,(ONO)]^+$	(+)	0	0	(+)
$[Coen_2(NO_2)Cl]^+$	(+)	(−)	(+)	(+)
$[Coen_2(NO_2)Br]^+$	(+)	(−)	(+)	(+)
$[Coen_2(NCS)Cl]^+$	$(+)_{5461}$	$(-)_{5461}$	$(-)_{5461}$	$(+)_{5461}$
$[Coen_2(H_2O)Cl]^{2+}$	(+)	(−)	(−)	(+)
$[Coen_2(H_2O)Br]^{2+}$	(−)	(−)	(−)	
$[Coen_2(H_2O)_2]^{3+}$	(+)	0	0	(+)
$[Coen_2Sal]^+$ (cf. footnote g)	(−)	0	(+)	(+)
$[Rhen_2Cl_2]^+$	$(-)_{5350}$	0	0	(−)
$[Iren_2(NO_2)_2]^+$	0	(+)	0	(−)

[a] (+)BCS = α-bromo(+)camphorsulphonate. [b] (+)CS = (+)camphorsulphonate. [c] (+)SbOT = (+)antimonyl tartrate. [d] The sign in this column is that of the enantiomer with the D absolute configuration. [e] O indicates no resolution. [f] The sign of rotation is that of the enantiomer forming the less soluble diastereoisomer with the given anion. [g] Sal = salicylate.

of other trivalent metals. For example the isomorphous less soluble diastereoisomers are D(+) $[\mathrm{Coen_2Cl_2}]$(+)BCS, and (+) $[\mathrm{Cren_2Cl_2}]$(+)BCS; the (+)dichloro complex of chromium(III) therefore has the D configuration.

The results discussed in this paper are collected in Table II and in Fig. 5, which shows the interconversions of the optically active complexes which have been effected in this work.

REFERENCES

1 R. D. Gillard, E. D. McKenzie, R. Mason, S. J. Mayhew, J. L. Peel and J. Stangroom, *Nature*, 208 (1965) 769.

2 K. Nakatsu, *Bull. Chem. Soc. Japan*, 35 (1962) 862.

3 R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, (1964) 1368.

4 J. H. Dunlop, R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, (1964) 3160.

5 J. H. Dunlop and R. D. Gillard, *J. Inorg. Nucl. Chem.*, 27 (1965) 361.

6 T. S. Piper, *J. Am. Chem. Soc.*, 83 (1961) 3908.

7 R. Dingle, *Chem. Commun.*, 1 (1965) 324.

8 (a) J. P. Mathieu, *Bull. Soc. Chim. France*, 4 (1937) 687. (b) T. E. MacDermott and A. M. Sargeson, *Australian J. Chem.*, 15 (1963) 334.

9 A. Werner, *Z. Anorg. Chem.*, 22 (1900) 91.

10 K. Schug and M. J. Gilmore, *Proc. 7th Intern. Conf. Coord. Chem., Stockholm*, (1962) 274.

11 W. C. Waggener, J. A. Mattern and G. H. Cartledge, *J. Am. Chem. Soc.*, 81 (1959) 2958.

12 R. K. Murmann and H. Taube, *J. Am. Chem. Soc.*, 78 (1956) 4886.

13 R. K. Murmann, *J. Am. Chem. Soc.*, 77 (1955) 5190.

14 P. J. Staples, *J. Chem. Soc.* (1964) 2320.