Five-co-ordinate Organocobalt(III) Complexes; Balanced Valency and Stereochemistry

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THE qualitative idea that the catalytic activity of transition-metal complexes is related to an easily variable geometry and valency is widely accepted, though it has been difficult to demonstrate the relevant points in a single set of complexes and in the absence of complicating factors. We have been using corrinoids (cobalt complexes related to vitamin B_{12}), where one can vary a single ligand, to study *cis*- and *trans*-effects.[1] We now report the existence of equilibria between six- and five-co-ordinate cobalt(III) corrinoids and comment on the balance between formal valencies in relation to reaction mechanisms and catalytic properties.

Many of the complexes where one axial ligand (X) is a carbon-ligand and the other (Y) is H_2O show large and reversible changes in spectrum (1) on heating the solution in water or methanol and (2) on drying the solid, the amount of change depending on the nature of X (see below). These changes involve a decrease in the $\alpha\beta$ bands at 490—530 mμ and the γ-band at 350—380 mμ, and the rise of other bands at 450—470 and 300—320 mμ; when $X = NC^-$ only the first type of spectrum is observed, when $X = Me_2CH^-$ only the second, all the others showing a mixture. The changes in (1) and (2) correspond to the same equilibria, as shown by the identity of the isosbestic points and absorption bands, and establish that water is involved in the equilibrium; since these complexes only dissolve in donor solvents which appear to behave similarly to water, the role of water cannot be studied in solution. Comparison of the spectra in air and argon and in trifluoroacetic acid, which is known to protonate amides,[2] shows that the equilibrium does not involve the amide side-chains or gases such as O_2 or N_2. The τ value of the ^1H n.m.r. of the methene hydrogen at C-10 in the corrin ring changes with the spectrum (*e.g.*, for X = vinyl in MeOH from 3·61 at $-60°$ to 3·31 at $+50°$, in water from 3·35 at $+23°$ to $+3·17$ at $+90°$). We conclude that the observed changes correspond to the equilibrium

$$[\mathrm{Co^{III}{\cdot}corrin{\cdot}X}] + \mathrm{H_2O} = [\mathrm{Co^{III}{\cdot}corrin{\cdot}X{\cdot}H_2O}]$$

between a six-co-ordinate aquo-complex and a five-co-ordinate square-pyramidal complex. The equilibrium constant depends on X, the following qualitative order being found for aqueous solutions at room temperature: $\mathrm{NC^-}$ (~100% six-co-ord.) > vinyl$^-$ (~30%) > $\mathrm{CH_3^-}$ (~10%) > $\mathrm{MeCH_2^-}$ (~0%, but formed at lower temp.) > $\mathrm{Me_2CH^-}$ (~0% even at low temp.). The order of ligands is the same as that previously found for *cis*- and *trans*-effects.[1] The value of $\Delta H = -3·5 \pm 1$ kcal./mole was obtained from the variation of the ^1H n.m.r. of the vinyl complex. Spectroscopic studies have also shown that the biologically important coenzyme (where X is a substituted ethyl group) exists in solution as a mixture of five- and six-co-ordinate complexes with Y = H_2O and benzimidazole.

Strong evidence has been obtained for analogous equilibria in cobalt(III) complexes containing the ligands bis(acetylacetone)ethylenediamine or bis-(salicylaldehyde)ethylenediamine when $X = \mathrm{CH_3^-}$, *etc.*, and Y = H_2O;[3] the dehydration of the corresponding bis(dimethylglyoxime) complexes may be similar.[4] A delicate balance of configurations seems to be general for these alkyl–cobalt(III) complexes. A balance between five- and six-co-ordinate complexes (and dimers with metal–metal bonds) also exist in low-spin cobalt(II) cyanide and isocyanide complexes;[5,6] and, as already pointed out,[6] the similar values of the equilibrium constant for the substitution of benziminazole by H_2O on acidification in the cobalt(II) complex (pK_a ~2·5) and the methylcobalt(III) complex ($pK_a = 2·5$) show that the groups $[\mathrm{H_2O \rightarrow CO^{II}}]$ and $[\mathrm{CH_3^- \rightarrow Co^{III}}]$ place the same electron density on the cobalt, as seen by the other axial ligand. By merely varying one ligand, therefore, the stereochemistry and equilibrium constants can change from those typical of a cobalt(III) to those typical of a cobalt(II) complex, and the usual correlation between stereochemistry and valency and the division into valencies clearly breaks down. The division into valencies appears even less realistic when one considers the distribution of charge in the transition state. Good examples are provided by the methyl derivatives of the corrinoid,[7] pentacyanide,[8] and bisdimethylglyoxime[4] cobalt(III) complexes.

Cobalt(III) methyl complexes can be formed by the reaction of the $\mathrm{Co^I}$ complex with $\mathrm{CH_3I}$, *etc.*, (*i.e.*, $\mathrm{CH_3^+}$ in the transition state) or a $\mathrm{Co^{III}}$ complex with a Grignard reagent ($\mathrm{CH_3^-}$), and the methyl group can be removed by $\mathrm{Hg^{II}}$ or I_2 (as $\mathrm{CH_3^-}$) or liberated as a radical on heating or photolysis, *i.e.*, transition states are known corresponding to the formal valencies I—III:

$$\begin{tikzcd}[row sep=small] & {[\mathrm{Co^{II}\cdot\cdot CH_3}]} & \\ {[\mathrm{Co^{I}\cdot\cdot CH_3^+}]} \arrow[r, shift left] & {[\mathrm{Co{-}CH_3}]^{2+}} \arrow[u] \arrow[l, shift left] \arrow[r, shift left] & {[\mathrm{Co^{III}\cdot\cdot CH_3^-}]} \arrow[l, shift left] \end{tikzcd}$$

It is interesting that B_{12} derivatives are implicated in methyl transfer *in vivo*.[7] Reactions such as the formation of β-naphthylsulphamic acid from β-naphthylamine and $\mathrm{SO_3^{2-}}$ in the presence of corrinoids and O_2 or $\mathrm{CH_3I}$ to trap $\mathrm{Co^I}$[7] probably involve transition states corresponding to

$$[\mathrm{Co^{III}\cdot\cdot SO_3^{2-}}] \rightleftharpoons [\mathrm{Co{-}SO_3}]^+ \rightleftharpoons [\mathrm{Co^{I}\cdot\cdot SO_3}]$$

These complexes, therefore, provide a simple demonstration of (1) a balance between different configurations, (2) the unreality of any rigid distinction between valencies in the ground state, and (3) the variation between formal valencies attainable in the transition state. The term "balanced valency" might be used to describe the situation in (2). Similar ideas are discussed by Vallee and Williams in connection with certain metal-containing enzymes.[9]

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