Metal–Ligand Interactions in Cobalt(III) Complexes derived from Vitamin B_{12}

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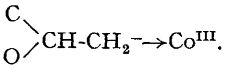
VITAMIN B_{12} and its derivatives [octahedral cobalt(III) complexes containing the corrin ring as the planar ligand] provide a useful series of compounds with which to study interactions between ligands transmitted through the metal atom (*cis*- and *trans*-effects).[1,2] These interactions have been subdivided,[2] in order of diminishing ease of interpretation, into ground-state (*e.g.*, bond lengths and force constants within one complex), thermodynamic (equilibrium constants between two complexes), and kinetic effects. In most studies of the *trans*-effect, particularly with square-planar platinum(II) complexes, emphasis has been placed on the kinetic aspects.[3] Previous work on the *trans*-effect in vitamin B_{12} complexes,[1,2] however, has been concerned with the effect of changing one axial ligand on the equilibrium constants for substitution reactions in the *trans*-position (thermodynamic effect).

We have now studied the effect of changing the axial ligand on the infrared stretching frequency of cyanide co-ordinated in the *trans*-position (see Table; axial ligand designated X). Ligands co-ordinated through carbon predominate because they are relatively stable kinetically and provide a series with identical charge and ligand atom but with varying electronegativity. In the case of 5′-deoxyadenosyl the atoms of interest are



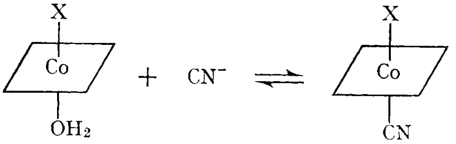
$\left.\begin{array}{l}\mathrm{C}\\ \mathrm{O}\end{array}\right\rangle \mathrm{CH\text{-}CH_2^{-}\!\rightarrow Co^{III}}$. Hodgkin and co-workers[4,5] and Lenhert[6] have shown that the cobalt–ligand bond lengths depend on the nature of the axial ligand, and these results, together with further equilibrium constants (some of which have been briefly reported elsewhere[7]) are included in the Table. Cobalamins (in which the *trans*-ligand is the chelated 5,6-dimethylbenziminazole, abbreviated to BZ in the formulae) were used for the data in columns 2 and 5, and cobinamides (*trans*-ligand H_2O) for column 4. For details of the structure of these compounds see reference 1. The organocyanocobalamins (*trans*-ligand CN^-) used for column 3 were formed in the solid state by grinding the appropriate cobalamins with just sufficient KCN to cause displacement of the 5,6-dimethylbenziminazole by cyanide. KCl discs were used for recording the infrared spectra. A comparison of the reflection spectra of the solids with the absorption spectra in solution for dicyano-, vinylcyano- and methylcyano-cobalamins showed that in each case the same complex existed in both phases. The formation constants were determined in aqueous solution with $\mu \geqslant 0{\cdot}5$ at room temperature by spectrophotometry.

Varying just one ligand can clearly have an

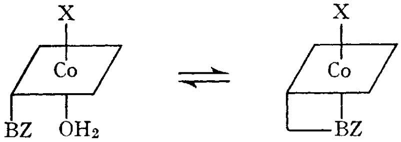
TABLE

(1) Axial ligand (X)	(2) Cobalt–BZ bond length (Å)	(3) CN⁻ stretching frequency (cm.⁻¹)	(4) Equilibrium constants[a,b] $\log_{10}K_{CN}$	(5) $\log_{10}K_{BZ}$
H_2O		2130	⩾14[f]	7·1[f]
$N{\equiv}C^-$	2·02[c]	2119	8[g]	4·6[f]
$HC{\equiv}C^-$		2110	—	4·0[f]
$CH_2{=}CH^-$		2093	2·7	2·3[f]
CH_3^-		2088	2·1[h]	2·2[f]
5′-Deoxyadenosyl⁻	2·23[d]	2091[e]	[e]	1·3[f]
$CH_3{\cdot}CH_2^-$		2082	0·6	0·8[i]

[a] K_{CN} is the equilibrium constant (in l./mole) for



[b] K_{BZ} is the equilibrium constant (as the ratio) for



[c] Average of the values for wet (1·97 Å) and dry (2·07 Å) vitamin B_{12}; refs. 4 and 5, respectively. [d] Ref. 6. [e] The cobalt–alkyl bond is rapidly decomposed by cyanide in water, but is stable in dimethyl sulphoxide solution and in the solid state. [f] Ref. 1. [g] Ref. 8. [h] More accurate value than that given in ref. 1. [i] Ref. 9.

extremely large effect on the bonding in the *trans*-position, *e.g.*, K_{CN} changes by a factor of at least 10^{13}. With the exception of the slight discrepancy shown by the 5′-deoxyadenosylcobalamin, the stretching frequencies and the two sets of equilibrium constants all show the same order of dependence on the axial ligand. The results show that, as the axial ligand becomes more polarisable (H_2O, $N{\equiv}C^-$, . . . $CH_3{\cdot}CH_2^-$) so the *trans*-metal–ligand bond length increases, the *trans*-ligand itself becomes more ionic (*cf.*, free CN⁻, 2079 cm.⁻¹) and the values of the formation constants approach those expected for ion-pairs with non-transition metals (*i.e.*, low values with no marked preference for carbon or nitrogen as the ligand atom). We conclude that the predominant factor operating in both the ground-state and thermodynamic effects is the amount of charge donated to the cobalt atom *via* the σ-bond. Vitamin B_{12} and its derivatives appear to be the first set of complexes in which these two effects have been examined together.

It should be pointed out that strong *cis*-effects also occur in these complexes, as shown by the influence of the axial ligand on the π–π^* transitions of the corrin ring[10,2] and on the bond lengths between cobalt and the equatorial nitrogen atoms.[4–6] In the organocyanocobalamins the change in the energies of the π–π^* transitions parallel the change in the stretching frequency of the co-ordinated cyanide; this will be discussed later in further detail.

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