The Chemistry of Vitamin B_{12}. Part 28.[1] Crystal Structure‡ of Dicyanocobyrinic Acid Heptamethyl Ester and its Interaction with Alcohols: the Effects of Hydrogen Bonding to Co-ordinated Cyanide

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An *X*-ray structural analysis of the Pr^{i}OH adduct of dicyanocobyrinic acid heptamethyl ester [monoclinic, space group $P2_1$, a = 16.332(6), b = 13.252(5), c = 14.475(5) Å, β = 109.75(3)°, and Z = 2] has shown that one cyanide is H-bonded to the Pr^{i}OH while the other interacts with two methyl groups of ester side-chains on neighbouring molecules. A study of the solvent dependence of the absorption spectrum of the dicyanide has shown that the wavelength of the main (γ) band varied from *ca.* 374 nm in non-polar solvents (*e.g.* benzene, CCl_4) through *ca.* 371 nm in more polar solvents (MeCN, $MeCO_2Me$), to *ca.* 368 nm in protic solvents [H_2O, ROH (R = alkyl)], accompanied by an increase in the CN stretching frequency, while the titration of a solution of the dicyanide in CCl_4 with MeOH showed the binding of one molecule of MeOH per Co with K_1 = 7 dm^3 mol^{-1} and a further equilibrium with $K_2 \leqslant$ 0.05 dm^3 mol^{-1}. The results show that H-bonding to co-ordinated cyanide reduces the donor power of the ligand towards the metal, with effects on both the *cis* and *trans* positions, and also suggests that interaction with a methyl carrying a slight positive charge (as in MeCN and $MeCO_2Me$) is qualitatively similar to, though weaker than, an H-bond.

The properties of co-ordinated cyanide are very sensitive to electronic changes within the metal complex (see, for example, the effects on the cyanide stretching frequency in Co^{III} complexes);[2–5] we have exploited these 'internal' effects in studying and correlating the *trans* effect in Co^{III} corrinoids at the ground-state, thermodynamic, and kinetic levels.[6] There is a considerable amount of evidence in the literature which indicates that the properties of co-ordinated cyanide are also unusually sensitive to changes in the outer co-ordination sphere, both in the solid state (*cf.* the variation in CN stretching frequency with the nature of the matrix)[7] and in solution (see below); the study of these 'external' effects in Co^{III} corrinoids is the subject of the present paper. In addition, there is currently great interest in studying the occurrence and effects of H-bonds involving the N–H bond of the co-ordinated imidazole ring in iron porphyrin complexes, prompted by the suggestion that the protein may moderate the activity of the Fe atom in haemoproteins through changes in the H-bond to the co-ordinated imidazole ring of histidine; see, for example, two recent papers[8,9] and the references therein. Studies on the effects of H-bonding *to* co-ordinated cyanide in Co^{III} corrinoids are obviously complementary to studies on H-bonding *from* co-ordinated imidazole in Fe^{III} porphyrins.

Varying the solvent has been shown to have a significant effect on (*i*) the *d–d* transitions of the $[Co^{III}(CN)_6]^{3-}$ ion (*e.g.* from 311 nm in H_2O to 318 nm in MeCN and 321 nm in dmso§)[10] with accompanying changes in the CN stretching frequency (from 2 127 cm^{-1} in H_2O to 2 111 cm^{-1} in dmso)[11] and the ^{59}Co n.m.r. spectra[10] (also used to study its interaction with cations, H-bonding solutes and proteins[12–16]), (*ii*) the CN stretching frequency of $[Fe^{III}(CN)_6]^{3-}$,[11] (*iii*) the metal-to-ligand charge transfer bands in $[Au^I(CN)_2]^-$,[17] (*iv*) the electronic spectrum of $[Fe^{II}(phen)_2(CN)_2]$[18–20] (probably the *cis*-isomer,[21,22] transitions assigned as charge transfer[21]) and related complexes,[20] (*v*) the n.m.r. and electronic spectra of dicyanoiron(III) porphyrin complexes,[23] and (*vi*) the electronic spectra of dicyanocobalt(III) corrinoid[24] and dicyanocobalt(III) tetradehydrocorrinoid[25,26] complexes, and of cyanocobalamin (vitamin B_{12})[27,28] where the spectra correspond to π–π transitions within the conjugated ring.[29a] Unspecified solvent effects on the CN stretching frequency of $Hg(CN)_2$ have also been noted.[30] The observed effects are clearly due to direct interaction between the solvent and the co-ordinated cyanide in the hexacyanides, as has also been shown for $[Fe^{II}(phen)_2(CN)_2]$,[18] but this remains to be established for the porphyrins and corrinoids.

Two main questions arise, *viz.* (*i*) are the observed solvent effects due mainly to specific (*e.g.* H-bonding) interactions between the co-ordinated cyanide and a solvent molecule or to a more general change in the microenvironment around the ligand, and (*ii*) are these effects relayed to the metal through changes in the σ-donor or π-acceptor properties of the cyanide ligands? The second question will be discussed in a later paper. A non-specific solvent effect is suggested by the facts that (*i*) there is a positive correlation between the observed shift in wavelength and the $E_T(30)$ and/or Z value of the solvent[31] for vitamin B_{12},[28] the dicyanocorrinoid,[24] and the tetradehydrocorrinoid,[25] (*ii*) isosbestic points have not been observed as the solvent composition is varied,[18] (*iii*) the CN stretching frequency of co-ordinated isocyanides (with no lone pair on the terminal N atom to form H-bonds) shows a solvent dependence,[32] and (*iv*) ^{59}Co n.m.r. studies failed[10] to distinguish any individual steps in the interaction of $[Co(CN)_6]^{3-}$ with H-bonding solutes. *X*-Ray structural studies on Co corrinoids, on the other hand, have demonstrated the strong tendency of co-ordinated cyanide to form specific H-bonds, at least in the solid state.[29b] It is, of course, possible that the H-bonds observed in the crystalline state are disrupted in solution by thermal energy. Tests are therefore needed for the formation

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§ Abbreviations: dmso = dimethyl sulphoxide, phen = 1,10-phenanthroline, C_6H_{11} = cyclohexyl, dcc = dicyanocobester, mc = methylcobester, chc = cyclohexylcobester, vitamin B_{12} = cyanocobalamin, dbzm = 5,6-dimethylbenzimidazole.

of specific H-bonds in solution (through the observation of isosbestic points as the concentration of, *e.g.*, an alcohol is increased) and for the occurrence of other specific interactions (*e.g.* with a methyl group carrying a slight positive charge as in MeCN) both in the solid state (*X*-ray analysis) and in solution (isosbestic points).

The naturally occurring corrinoids all possess hydrophilic side-chains which restrict their solubility to the more polar solvents (water, lower alcohols, dmso), but the range of possible solvents can be extended by conversion of the amide side-chains into esters.[24,33] The aim of this paper is further to investigate the basis of these 'external' effects on co-ordinated cyanide by studying dicyanocobyrinic acid heptamethyl ester or 'dicyanocobester'[33] (dcc), where the absence of overall net charge precludes complications due to ion pairing, both in solution (in solvents ranging from water to benzene) and in the solid state (as the adduct with Pr^iOH). This extends previous work on the heptapropyl homologue in solution (studied in various solvents from MeOH to benzene but not in H_2O, in which it is insoluble)[24] and *X*-ray determinations of the anhydrous[34] and monohydrated[35] forms of dcc, and serves to link together much of the scattered evidence of 'external' effects on co-ordinated cyanide.

Experimental

Materials.—Samples of vitamin B_{12} were kindly given by Mr. A. P. Domleo of Glaxo-Allenbury (Pty) Ltd. All solvents were AnalaR grade and used as received except CCl_4 which was dried by treating with activated 4A molecular sieves and MeOH which was dried by distillation from metallic sodium.[36] Precautions against photolysis were taken when handling all solutions of corrinoids.

Preparation of 'Cobester' Derivatives.—The dicyanide (dcc) was prepared by Werthemann's method,[33] *i.e.* by refluxing a *ca.* 6×10^{-3} mol dm^{-3} solution of vitamin B_{12} in methanol containing 1 mol dm^{-3} H_2SO_4 under N_2 for 4 d, followed by concentration, dilution with water, neutralisation ($NaHCO_3$) and treating with KCN to form the purple dicyanide, which was extracted first with CCl_4 and then with CH_2Cl_2 and the solvent removed. The solid was dissolved in benzene (we also used toluene), chromatographed on silica gel containing KCN and eluted with benzene- or toluene–methyl acetate (2:3), which left other products at the top of the column. Removal of the solvent gave the product as red-violet crystals whose purity was demonstrated by t.l.c. using a silica-gel plate, which had been sprayed with a saturated solution of KCN in methanol, with benzene–methyl acetate (1:4) as a solvent.

Werthemann[33] converted the dicyanide (dcc) to the alkyl derivatives by a method involving several stages including isolation of the monocyanide as a solid. However, in the case of the methyl derivative n.m.r. spectroscopy suggested the presence of only one axial isomer while t.l.c. revealed the presence of four orange components (presumably all Co–Me complexes) as well as a reddish corrinoid; attempts to separate the compounds by column chromatography were unsuccessful. We adopted the following simplified method of preparing alkyl derivatives. The dicyanide (20 mg) was first dissolved in methanol (5 cm^3), then diluted with 2×10^{-4} mol dm^{-3} aqueous $Co(NO_3)_2$ (20 cm^3). The purple solution was deoxygenated (stream of N_2) and reduced with a small quantity of $NaBH_4$ to give a green solution of the Co^I complex. This was treated with an alkylating agent (*e.g.* MeI, 100 μl) and allowed to stand in the dark (from 10 min for the Co–Me to 30 min for the Co–C_6H_{11} complex) to give a yellow solution of the alkyl derivative. The cobalt nitrate is required as a catalyst for reduction by tetrahydroborate[37] and the concentration used was the minimum necessary to give convenient rates; higher concentrations tended to cause problems in purification. Purification of mc and chc involved shaking the aqueous solution with portions of benzene and toluene to extract any unreacted purple dcc and also some unidentified red corrinoid, followed by extraction into Bu^nOH (leaving the inorganic impurities in the aqueous phase). One fraction of the yellow alkyl derivative could not be extracted, presumably due to hydrolysis of one or more ester side-chains. The solvent was removed by evaporation at room temperature in a stream of air to leave a brown solid. Tests for solubility showed that the methyl and cyclohexyl complexes dissolved in solvents such as water, the lower alcohols, methyl acetate, and CH_2Cl_2 but not in diethyl ether, benzene, or toluene. T.l.c. of the cyclohexyl product (on silica gel with methanol) revealed the presence of two main spots (presumably both Co–C_6H_{11} complexes), sometimes followed by a long yellow-pink streak (probably due to hydrolysis of an ester side-chain occurring on the plate). Attempts to separate the components by column chromatography (silica-gel column, eluting with Bu^nOH–MeOH mixtures) merely accelerated the presumed hydrolysis of the side-chains. If an aqueous solution of the mixture was photolysed in the presence of air and cyanide, then t.l.c. (on silica gel with methanol) showed the presence of one main purple spot with the same R_f value (0.8) as the original dicyanide complex (hence both the main yellow spots probably have the same side-chains but differ in the orientation of the alkyl ligand), together with a minor slower-moving (R_f 0.7) spot (presumably reflecting hydrolysis of a side-chain). The methyl complex showed similar complex behaviour, as did several other alkyl derivatives not directly relevant to the present work.

U.v.–Visible Spectra.—These were recorded with a Cary 2300 spectrophotometer in 1-cm cells at 25 °C. To obtain the solvent-dependence data identical volumes of a stock solution of dcc in CCl_4 were injected into an empty cell, the CCl_4 allowed to evaporate, and the required solvent (2 cm^3) added to dissolve the film of dcc.

I.r. Spectra.—The i.r. spectra of dcc in organic solvents were recorded on a Perkin-Elmer 580B i.r. spectrometer between NaCl plates.

X-Ray Structure Analysis of Dcc.—*Crystal data.* $C_{54}H_{73}CoN_6O_{14}\cdot C_3H_8O$, $M = 1\,149.25$, monoclinic, space group $P2_1$, $a = 16.332(6)$, $b = 13.252(5)$, $c = 14.475(5)$ Å, $\beta = 109.75(3)°$, $U = 2\,948.6$ Å^3, $Z = 2$, $F(000) = 1\,223.98$, $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å, $\mu(\text{Mo-}K_\alpha) = 3.18$ cm^{-1}.

The density was found to be 1.23 g cm^{-3} using a concentrated aqueous solution of RbCl (the crystals were slightly soluble in common organic solvents), which is less than the calculated value of 1.29 g cm^{-3} (probably due to replacement of Pr^iOH in the crystal lattice by H_2O).

Data collection. A suitable crystal, of approximately rhombic prismatic shape and of dimensions *ca.* $0.55 \times 0.35 \times 0.30$ mm, was mounted on a glass fibre with Shelac. Data were collected with a Philips PW 1100 four-circle diffractometer with a graphite monochromator using Mo-K_α radiation, under the following conditions. Scan mode, ω–2θ; scan width, 1.300°; scan speed, 0.052° s^{-1}. Measured intensities, 4 324; unique reflections, 4 265. Cut off criteria, $F > 2\sigma(F)$; observed intensities, 4 118. The data were corrected for Lorentz polarization effects, but not for absorption, as the absorption coefficient was small.

Solution of the structure. The crystal structure was solved using standard Patterson and Fourier techniques, employing the heavy-atom method for phase determination in the early stages. The origin was defined by fixing the *y* co-ordinate of the cobalt atom. Full-matrix least-squares refinement for all non-hydrogen atoms, using an anisotropic thermal parameter for the cobalt atom, gave a final conventional $R = 0.1146$, using the SHELX program.[38] Complex scattering factors were used[39] and unit weights were employed throughout the analysis. Friedel pairs were not measured and therefore the solution does not assign the absolute configuration of the molecule.

Results

X-Ray Structural Analysis of Dcc.—The unit cell contains two molecules of the uncharged dcc related by a two-fold screw axis parallel to the *b* axis of the unit cell. Each dcc molecule has a molecule of Pr^{i}OH (origin not definitely established) H-bonded to the cyanide co-ordinated in the lower (α) position (*cf.* the comments on p. 17 of ref. 33 regarding the 'irreversible' incorporation of organic molecules into the lattice). None of the methyl ester side-chains has been hydrolysed or undergone epimerisation (relative to their orientation in B_{12}). Selected bond lengths and angles relevant to the Co co-ordination sphere and the Pr^{i}OH molecules are listed in Table 1. Final atomic co-ordinates are given in Table 2. The numbering scheme is shown in Figure 1 and an ORTEP diagram given in Figure 2. The geometry of the corrin ring and the relative orientation of the side-chains are shown by the cylindrical projection in Figure 3, as viewed from the central Co atom outwards. The structure is most conveniently discussed in four sections working out from the centre: *viz.* (*i*) the NC–Co–CN unit and its interactions, (*ii*) the corrin ring and its four co-ordinated N atoms, (*iii*) the side-chains, and (*iv*) intermolecular contacts and the packing of the molecules in the crystal.

The cyanide co-ordinated in the lower (α) axial position is H-bonded to a molecule of Pr^{i}OH with a N ··· O distance of 2.74 Å, while that in the upper (β) position is in contact with the methyl groups of two propionate side-chains (see below). The Co–C and C–N bond lengths (see Table 1) are typical for cyanocorrinoids (*cf.* ref. 34). The four co-ordinated N atoms of the corrin ring show a slight tetrahedral deviation from the mean plane, the conjugated corrin ring shows a distinct 'bowing' about the C(5)–C(35) axis (see Figure 3), and all the pyrrole rings are puckered (A, B, and D with an 'envelope' conformation, C with a 'half-chair' conformation); these features are typical of all other corrinoids studied (see the summary in ref. 34). The cylindrical projection (Figure 3) shows that there are no significant differences in the orientation of the side-chains between dcc and other corrinoids; the three ethanoate groups project above the plane of the ring and the four propionate

Table 1. Selected structural data for dcc

Bond lengths (Å)			
(*i*) Co-ordination sphere		(*ii*) Pr^{i}OH molecules	
Co–N(21)	1.892(11)	O(75)–C(77)	1.390(25)
Co–N(22)	1.919(10)	C(76)–C(77)	1.600(32)
Co–N(23)	1.931(12)	C(77)–C(78)	1.712(32)
Co–N(24)	1.915(11)	(*iii*) Bonds to co-ordinated CN	
Co–C(64)	1.923(15)	N(67) ··· O(75)	2.74
Co–C(66)	1.924(15)	N(65) ··· C(E72)	3.21
C(64)–N(65)	1.127(20)	N(65) ··· C(E73)	3.18
C(66)–N(67)	1.171(19)		
Bond angles (°)			
(*i*) Co-ordination sphere		(*ii*) Pr^{i}OH molecules	
N(21)–Co–N(22)	91.4(4)	O(75)–C(77)–C(76)	109.6(1.9)
N(21)–Co–N(24)	82.9(5)	O(75)–C(77)–C(78)	111.2(1.8)
N(22)–Co–N(23)	95.0(5)	C(76)–C(77)–C(78)	111.1(1.8)
N(23)–Co–N(24)	90.9(5)	(*iii*) Bonds to co-ordinated CN	
Co–C(64)–N(65)	176.2(14)	N(67)–O(75)–C(76)	100.5
Co–C(66)–N(67)	178.4(14)	C(64)–N(65)–C(E72)	108.2
		C(64)–N(65)–C(E73)	105.6

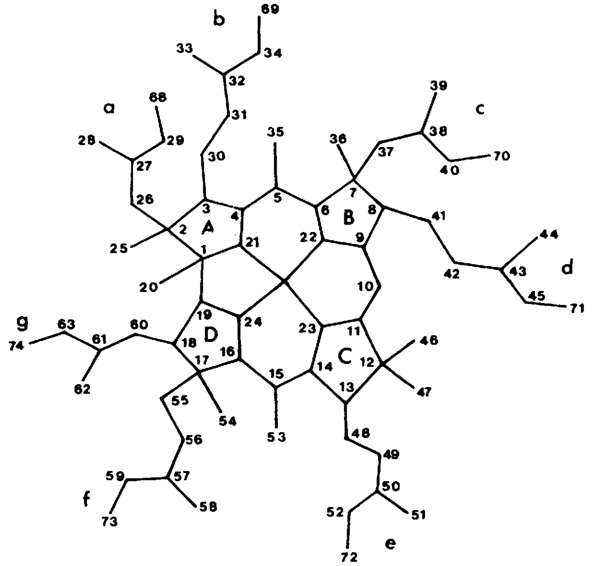

Figure 1. Atom numbering scheme for the corrinoid molecule dcc, together with the lettering of the pyrrole rings (A—D) and of the side-chains (a—g). The upper (β) cyanide atoms are numbered C(64) and N(65), the lower (α) C(66) and N(67); the atoms of Pr^{i}OH are numbered O(75) and C(76)—C(78). Methyl ester groups are denoted by E, *e.g.* C(E68)

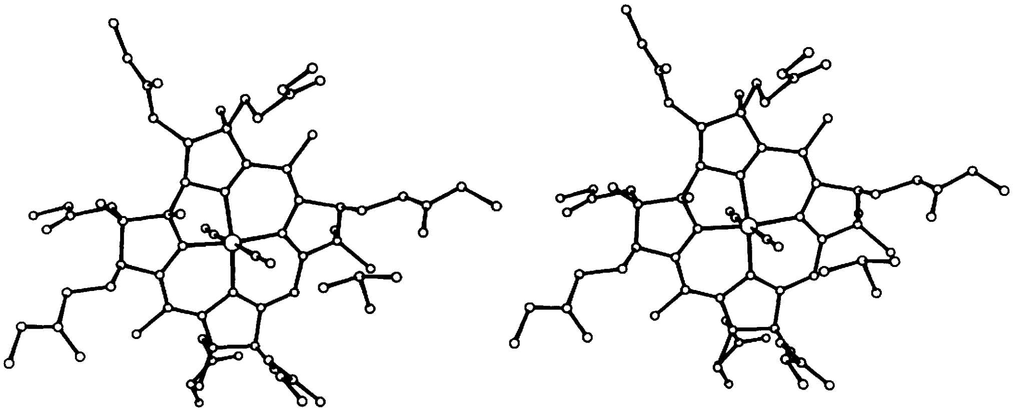

Figure 2. ORTEP diagram of the dcc molecule

Table 2. Final fractional atomic co-ordinates (× 10^4) for dcc

Atom	*x*	*y*	*z*
Co	2 605(1)	2 500	2 284(1)
C(1)	3 973(8)	3 642(11)	1 955(9)
C(2)	4 140(8)	4 093(11)	1 023(9)
C(3)	3 236(8)	4 572(10)	422(9)
C(4)	2 640(8)	3 943(10)	775(9)
C(5)	1 618(8)	3 876(10)	254(9)
C(6)	1 157(8)	3 363(10)	613(9)
C(7)	173(9)	3 177(11)	92(10)
C(8)	−113(8)	2 771(11)	956(9)
C(9)	743(8)	2 339(11)	1 646(9)
C(10)	757(9)	1 643(11)	2 345(10)
C(11)	1 518(9)	1 275(12)	3 043(10)
C(12)	1 494(10)	499(13)	3 804(11)
C(13)	2 428(9)	627(11)	4 576(10)
C(14)	2 923(8)	1 122(10)	3 957(9)
C(15)	3 794(8)	1 154(11)	4 247(9)
C(16)	4 242(9)	1 697(11)	3 658(10)
C(17)	5 213(9)	1 680(11)	3 804(10)
C(18)	5 281(8)	2 588(13)	3 141(9)
C(19)	4 356(8)	2 642(12)	2 363(9)
C(20)	4 159(10)	4 465(12)	2 791(11)
N(21)	3 025(7)	3 447(9)	1 573(8)
N(22)	1 422(6)	2 775(8)	1 489(7)
N(23)	2 308(7)	1 539(9)	3 124(8)
N(24)	3 818(7)	2 233(9)	2 918(8)
C(25)	4 911(10)	4 818(13)	1 284(11)
C(26)	4 307(9)	3 202(12)	403(11)
C(27)	4 340(10)	3 501(14)	−617(12)
O(28)	4 330(9)	4 328(12)	−949(10)
O(29)	4 369(8)	2 683(12)	−1 088(9)
C(30)	3 092(10)	5 716(13)	549(11)
C(31)	3 367(11)	6 325(14)	−191(12)
C(32)	2 984(10)	7 354(14)	−296(11)
O(33)	2 316(11)	7 599(17)	−129(11)
O(34)	3 396(8)	8 074(10)	−567(9)
C(35)	1 344(10)	4 412(12)	−741(11)
C(36)	−396(10)	4 084(13)	−418(11)
C(37)	137(9)	2 281(12)	−621(10)
C(38)	−741(10)	1 826(13)	−1 118(12)
O(39)	−1 027(8)	1 135(11)	−785(9)
O(40)	−1 153(8)	2 257(10)	−1 975(8)
C(41)	−466(10)	3 550(13)	1 508(12)
C(42)	205(11)	4 339(14)	2 097(13)
C(43)	−150(11)	5 023(14)	2 706(12)
O(44)	−813(11)	4 884(15)	2 886(12)
O(45)	339(10)	5 787(13)	2 980(11)
C(46)	1 460(12)	−566(16)	3 340(13)
C(47)	696(12)	610(15)	4 180(13)
C(48)	2 476(10)	1 395(13)	5 424(12)
C(49)	2 434(12)	794(14)	6 322(13)
C(50)	2 328(11)	1 559(14)	7 075(12)
O(51)	2 066(10)	2 382(15)	6 941(11)
O(52)	2 516(9)	1 105(12)	7 934(11)
C(53)	4 336(10)	600(12)	5 183(11)
C(54)	5 423(10)	633(13)	3 476(11)
C(55)	5 824(10)	1 847(12)	4 887(11)
C(56)	5 556(11)	2 839(14)	5 311(13)
C(57)	5 952(11)	2 814(14)	6 485(13)
O(58)	5 938(8)	2 109(10)	6 999(9)
O(59)	6 307(9)	3 688(12)	6 776(10)
C(60)	6 011(9)	2 457(15)	2 684(10)
C(61)	6 887(10)	2 841(13)	3 383(12)
O(62)	6 998(9)	3 414(12)	4 031(10)
O(63)	7 518(7)	2 408(11)	3 140(8)
C(64)	2 584(9)	1 449(11)	1 359(10)
N(65)	2 540(10)	807(13)	835(12)
C(66)	2 533(9)	3 502(11)	3 216(11)
N(67)	2 481(9)	4 094(12)	3 795(10)
C(E68)	4 363(13)	2 799(17)	−2 119(15)
C(E69)	2 981(13)	9 064(17)	−816(15)
C(E70)	−1 980(14)	1 706(18)	−2 565(16)
C(E71)	110(15)	6 519(20)	3 602(17)
C(E72)	2 247(15)	1 730(20)	8 698(17)
C(E73)	6 663(16)	3 900(21)	7 828(18)
C(E74)	8 417(13)	2 763(17)	3 715(15)
O(75)	2 133(9)	5 203(12)	5 215(10)
C(76)	1 949(17)	4 870(22)	6 795(19)
C(77)	1 933(14)	4 436(18)	5 758(16)
C(78)	947(17)	3 901(23)	5 131(20)

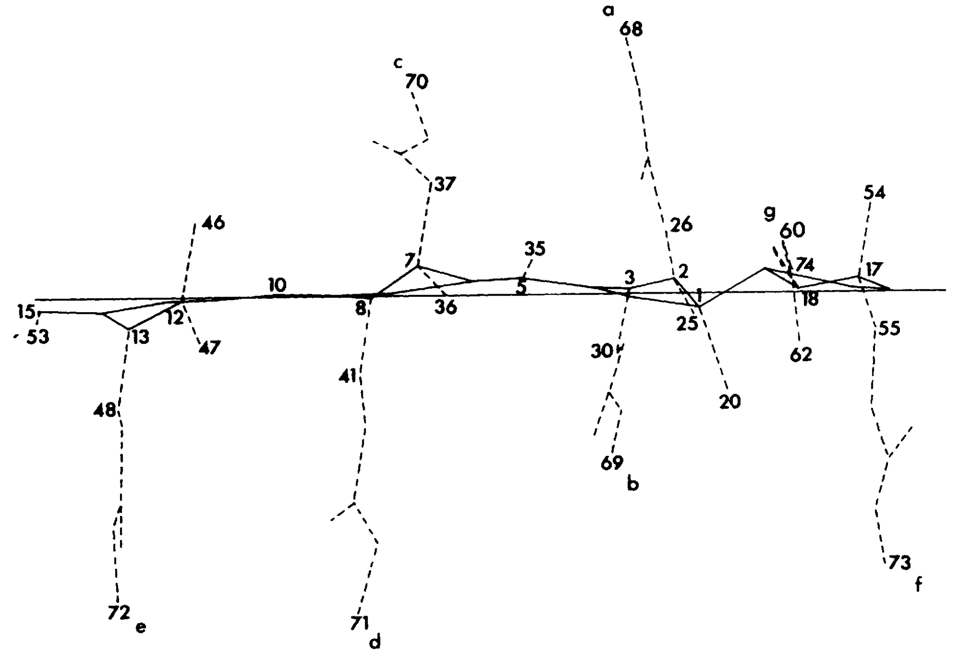

Figure 3. Cylindrical projection of dcc, viewed from the central Co atom outwards. The atoms are projected onto a cylinder of radius 2.8 Å and the vertical displacement corresponds to the distance from the mean plane through the four nitrogen atoms N(21)—N(24)

groups below the plane. With the exception of side-chain g on the ring D all the side-chains project in a direction roughly perpendicular to the corrin ring. Side-chain g projects outward and slightly upward with the first carbon atom [C(60)] above the mean plane, then bends down such that the carbonyl oxygen [O(62)] is situated at approximately the same level as, and at a distance of 4.6 Å from, the downward projecting methyl, C(20). Hydrogen bonding serves to link each Pr^{i}OH to a corrinoid molecule, but plays no part in holding the corrinoid molecules together. Each corrinoid is surrounded by six other corrinoids, one of which occupies the same unit cell. In addition to the numerous expected C–C and C–O intermolecular van der Waals contacts, there exists an additional and apparently significant web of contacts which involves the upper (β) cyanide. Interaction between the cyanide N of one molecule and the terminal methyl [C(E72)] of side-chain e on ring C of an adjacent molecule (x, y, $z + 1$), with a C $\cdots$ N distance of 3.21 Å, serves to link both molecules of the unit cell into chains along the c axis. Each molecule is also connected to its partner ($-x$, $y + \frac{1}{2}$, $-z$) in the same unit cell, roughly in a direction parallel to the a axis, by interaction between the cyanide N in one and the methyl group [C(E73)] of side-chain f on ring D in the other with a N $\cdots$ C distance of 3.18 Å.

Preparation of 'Alkylcobesters'.—We have developed a general method for the preparation of mc and chc from dcc which is simpler than that used previously[33] and have found, as already noted by Werthemann,[33] that most 'alkylcobesters' are produced as a mixture of components (probably involving both isomerisation of the axial ligands and hydrolysis of the side-chains) and that the use of both column and thin-layer chromatography is complicated by the ready hydrolysis of the side-chains (see Experimental section). Figure 4 shows that the spectra of chc (two main components, probably the two axial isomers) in water and in CH_2Cl_2 are very similar to each other and also (*cf.* Figure 8 of ref. 40) to that of the acidified cyclohexylcobalamin in water. This strongly suggests that the two (or more) components of chc have very similar spectra; similar arguments apply to the methyl analogues. We have therefore used the mixtures of components of chc and of mc without trying to develop methods for separating them and have examined their spectra in solvents ranging from water to CH_2Cl_2; the complexes are insoluble in solvents such as benzene and hexane.

Solvent Dependence of the Spectra of Dcc and other Corrinoids.—Table 3 includes published data, together with our observations on mc and chc and limited data on dcc, to show the effect of changing the side-chains (as between the cobalamins with amide side-chains and the 'cobesters') and/or the solvent (with no change in the nature of the axial ligands) on the wavelengths of the main absorption band in the four most important groups of corrinoid complexes, *viz.* (*i*) red, six-co-ordinate Co^{III} (here represented by the dicyanides), (*ii*) yellow, probably five-co-ordinate Co alkylcorrinoids (with methyl- and cyclohexylcorrinoids representing the forms[37] with maxima at *ca.* 460 and 440 nm respectively), (*iii*) yellow, probably five-co-ordinate Co^{II}, and (*iv*) green, probably four-co-ordinate Co^{I}. For the spectra of other dicyanocorrinoids where the $-CONH_2$ side-chains have been converted into, for example, $-CH_2OH$ or $-CH_3$ side-chains (both with λ_γ = 368 nm in MeOH) see ref. 41. The absence of any significant effect on the shape of the spectrum is shown for chc in Figure 4 and for dcc in Figure 5.

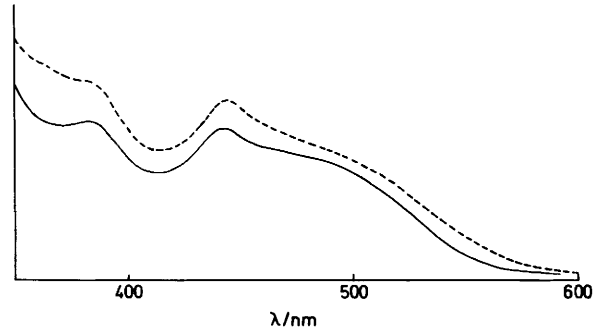

Figure 4. Comparison of the spectrum of chc (concentrations not identical) in H_2O (——) and CH_2Cl_2 (— — —)

The effects of a more extensive range of solvents on the spectrum of dcc alone are shown in Table 4. In all cases the spectra were recorded within 1 min of preparing the solution (see Experimental section) and remained unchanged for over 10 min. An analogous experiment with dmso showed that this solvent rapidly decomposed dcc to the monocyanide (λ_γ = 354 nm); the addition of solid KCN produced a colourless precipitate and did not suppress the decomposition of the dicyanide. The results show that an increase in $E_T(30)$ causes a fairly regular shift in all three bands (see Table 4 and Figure 6) to shorter wavelength, but with some obvious anomalies (see Discussion), and is accompanied (see Figure 5) by a fairly systematic movement of intensity from the lower into the higher vibrational bands within both the αβ and γ band systems and by a decrease in the DE system (around 400 nm).[29a] Molar

Table 3. Effect of varying the side-chains and the solvent on the spectra of Co corrinoids

Valency of Co and axial ligands	Corrinoid[a]	Solvent	$\lambda_{max.}$/nm	Ref.
NC–Co^{III}–CN	cobalamin/CN^-	H_2O	367—368	29*a*
	'cobester'	H_2O	368.1	*b*
		EtOH	369	33
			369.2	*b*
		benzene	373	33
			373.5	*b*
Co–Me	cobalamin/H^+	H_2O	460	37
	'cobester'	H_2O	464	*b*
		C_2H_4-$(OMe)_2$-1,2–	461	33
		H_2O(1:1)	456	33
		CH_2Cl_2	456	*b*
Co–C_6H_{11}	cobalamin/H^+	H_2O	442	37
	'cobester'	H_2O	442	*b*
		CH_2Cl_2	443	*b*
		$MeCO_2H$	442	*b*
		$MeCO_2Me$	441	*b*
Co^{II}–OH_2	cobalamin/H^+	H_2O	470	29*c*
Co^{II}–(?)[c]	'cobester'	EtOH	469	33
		benzene	469	33
		CH_2Cl_2	468	*d*
Co^{II}–N(dbzm)	cobalamin	H_2O	473	29*c*
Co^{II}–N(morpholine)	'cobester'	CH_2Cl_2	*ca.* 475.0[e]	*d*
Co^{I}	cobalamin	H_2O	388	50
		$MeCO_2H$	391	50
	'cobester'	diethyl ether–hexane (1:1)	394	33

[a] Cobalamin/H^+ or cobalamin/CN^- indicates that dbzm has been displaced from co-ordination through protonation of the N atom or the co-ordination of CN^- respectively. [b] This work. [c] Axial ligand not known. [d] Y. Murakami, Y. Hisaeda, and A. Kajihara, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 3642. [e] Estimated from Figure 2 of the reference in [d].

Table 4. Solvent dependence of the spectrum of dcc at 25 °C

Solvent	Solvent parameters[a] $E_T(30)$	Z	λ/nm (main bands)[b] γ	β	α
Toluene	33.9		373.9	553	592
CCl_4	32.5		373.7	553	592
Benzene	34.5	54	373.5	552	592
MeI			373.4	552	591
Chlorobenzene	37.5	58.0	373.3	551	591
Pyridine	40.2	64.0	372.0	550	590
CH_2Cl_2	41.1		371.7	550	589
Acetone	42.2	65.5	371.7	549	589
$CHCl_3$	39.1	63.2	371.5	549	588
$MeCO_2Me$	40.0		371.4	549	588
$MeNO_2$	46.3	71.2	*ca.* 371	548	586
MeCN	46.0	71.3	369.9	546	585
n-$C_5H_{11}OH$			369.6	546	585
Bu^nOH	50.2	77.7	369.5	545	584
Pr^nOH	50.7	78.3	369.5	546	585
EtOH	51.9	79.6	369.2	545	584
MeOH	55.5	83.6	368.8	543	582
H_2O[c]	63.1	94.6	368.1	542	581

[a] Values from ref. 31. [b] Errors of ±1 nm for the α and β bands and ±0.2 nm for the γ band, except in $MeNO_2$ where the solvent begins to absorb at *ca.* 370 nm. [c] With added KCN to suppress formation of the monocyanide.

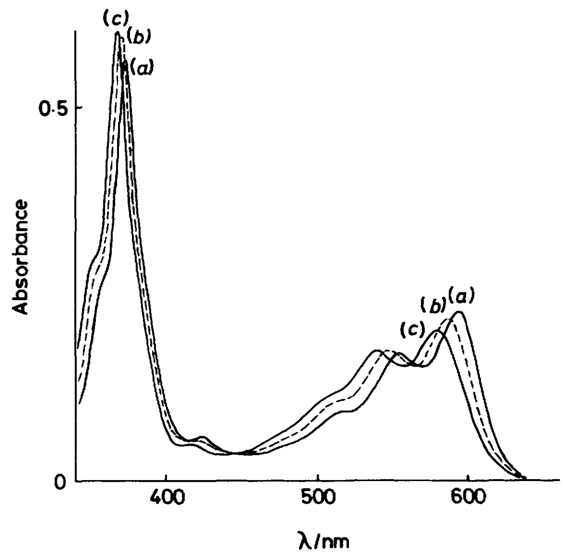

Figure 5. Comparison of the spectrum of 2.0 × 10^{-5} mol dm^{-3} solutions of dcc in (*a*) CCl_4, (*b*) MeCN, and (*c*) H_2O

absorption coefficients $A_{373.7}$ = 2.8 × 10^4 and $A_{368.1}$ = 3.0 × 10^4 dm^3 mol^{-1} cm^{-1} were determined in CCl_4 and H_2O respectively.

Titration of Dcc in CCl_4 *with* MeOH *and other Solvent Molecules*.—The possible effects of H-bonding to the co-ordinated cyanide were studied in CCl_4–MeOH mixtures where the equilibrium constant for formation of the H-bonded dimer of MeOH has a value of 2—3 dm^3 mol^{-1} (see Figure 4 of ref. 42); constants for the formation of higher aggregates have apparently not been determined, though the concentration of polymers probably exceeds that of the dimers at ⩾0.1 mol dm^{-3} MeOH.[42] Studies on H-bonding between dcc and MeOH in CCl_4 are therefore complicated by the existence of various other equilibria involving MeOH alone.

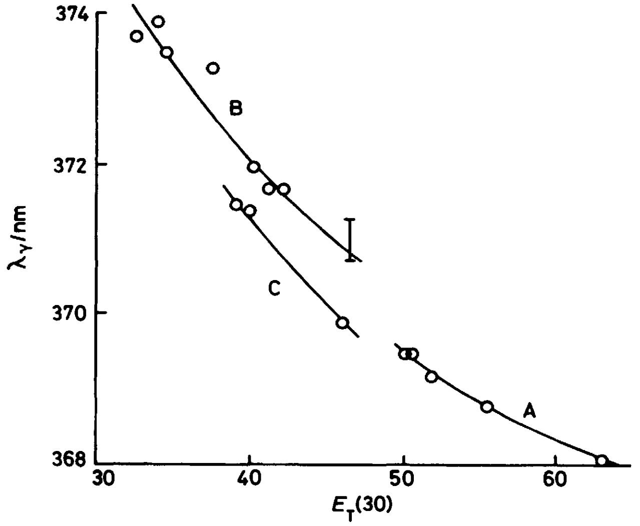

Figure 6. Variation of λ_γ of dcc with the $E_T(30)$ value of the solvent (data from Table 4); for an explanation of A—C see the Discussion

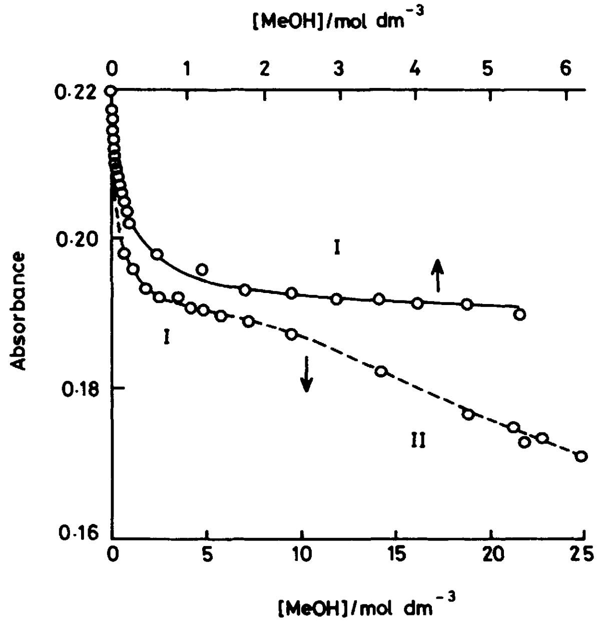

Figure 7. Spectrophotometric titration of a 2.0 × 10^{-5} mol dm^{-3} solution of dcc in CCl_4 with MeOH

Samples (2 cm^3) of a 2.0 × 10^{-5} mol dm^{-3} solution of dcc in CCl_4 (specially dried for experiment A, but used as received for experiment B) in a 1-cm spectrophotometer cell were titrated with MeOH (specially dried in both experiments) from a micro-syringe. The observed changes in $A_{592.5}$ for experiment A, corrected for dilution, are shown in Figure 7; all changes occurred instantaneously. Both experiments showed the existence of two main sections in the titration curve (labelled I and II in Figure 7) with the γ band at 369.9 nm in 20% MeOH and at 368.8 nm (see Table 4) in 100% MeOH; the spectrum in 20% MeOH is virtually identical to that in MeCN (see Figure 5). The changes in the spectrum associated with the first part of section I (where dcc could be titrated with MeOH with no significant change in volume) include four crossover points in the range

400—600 nm (*cf.* the four analogous crossover points between the spectra in CCl_4 and MeCN shown in Figure 5), with excellent isosbestic points at 455 and 565 nm and 'broken' isosbestic points at *ca.* 550 and 588 nm. It was not possible to prove or disprove the occurrence of isosbestic points in section II because of the small changes in the spectrum and the relatively large errors (in preparing the solvents of different composition and/or in correcting for volume changes during the titration). Further experiments showed (*i*) that the titration curves (as measured by the ratio of $A_{592.5}$ in 0 and 5 mol dm^{-3} MeOH) were independent of cobalt concentration over the range (0.6—5.0) × 10^{-5} mol dm^{-3} and (*ii*) that the observed changes did not involve dissociation of the di- to the monocyanide (no effect of adding KCN to dcc in 5 mol dm^{-3} MeOH).

Evaluation of the changes in $A_{592.5}$ for section I gave good linear plots of log ([dcc·MeOH]/[dcc]) *vs.* log $[MeOH]_T$ corresponding to the binding of one molecule of MeOH per Co with an apparent $K_1 = 7.2$ and 7.0 dm^3 mol^{-1} in the two experiments, where $K_1 = [dcc·MeOH]/[dcc][MeOH]_T$ and $[MeOH]_T$ indicates the total concentration of MeOH in all forms (monomer, dimer, oligomers); varying the value of A_∞ (for the end-point) showed that the best linearity was obtained with a value (0.193 in experiment A) close to the apparent end-point of section I (see Figure 7). Figure 7 suggests that section II requires ≥20 mol dm^{-3} MeOH for 50% completion, *i.e.* $K_2 \leqslant 0.05$ dm^3 mol^{-1}.

Qualitative experiments showed that the titration of dcc in CCl_4 with EtOH, Pr^nOH, Pr^iOH, and Bu^tOH all produced titration curves with two main sections similar to that with MeOH, but the experiments were complicated by the slow dissociation of dcc to the monocyanide (not observed with MeOH) and no quantitative titrations were therefore carried out. Attempts to prove or disprove the existence of isosbestic points in the titration of dcc in CCl_4 with MeCN or $MeCO_2Me$ were frustrated by the limited solubility of MeCN in CCl_4 and by the relatively small changes in spectrum observed on adding methyl acetate. In titrating dcc in acetone with MeCN, however, the early stages involved a fall in the γ-band region and an increase both above and below with definite crossover points at *ca.* 352 and 397 nm, though here again the changes in spectrum were too small relative to the possible error to prove or disprove the existence of true isosbestic points.

Solvent Dependence of the CN *Stretching Frequency of Dcc.*—The CN stretching frequency (±1 cm^{-1}) was observed at 2 117 cm^{-1} in CCl_4, 2 119 cm^{-1} in MeCN (observed on the side of the large band due to MeCN itself and corrected accordingly), 2 120 cm^{-1} in 1% MeOH–CCl_4 and 2 123 cm^{-1} in 18% (4.4 mol dm^{-3}) MeOH–CCl_4 (*i.e.* as the adduct with one MeOH per Co). The bandshape in 1% and 18% MeOH suggests that the observed band represents a single band and not the overlap of separate bands at 2 117 and ≥2 123 cm^{-1}, but similar conclusions could not be drawn about the band observed in MeCN. The CN band could not be observed in pure MeOH or $MeCO_2Me$ due to the high background absorption.

Discussion

X-Ray structural analyses have already been reported for dcc in its anhydrous form[34] and in a hydrated form with approximately one H_2O (disordered) per Co;[35] we have studied a solvate with one Pr^iOH (no detectable disorder) per Co. Our results (*i*) confirm the previous conclusion[34] that the structure of the cobalt–corrin ring is not significantly affected by changes in the environment (pattern of H-bonding, *etc.*), (*ii*) further demonstrate the strong tendency of co-ordinated cyanide to form H-bonds, even through the incorporation of polar molecules into a hydrophobic matrix, (*iii*) reveal the existence of apparently significant interactions between the co-ordinated (but not H-bonded) cyanide and methyl groups of the ester side-chains of neighbouring molecules, and (*iv*) focus attention on the unusual conformation of side-chain g.

The cyanide–methyl interactions observed in crystalline dcc resemble those discussed for crystalline MeCN;[43] they both represent interaction between a cyanide group carrying a slight negative charge and a methyl group carrying a slight positive charge. We also observe interactions between dcc and MeCN in solution, which are presumably analogous (see below). We suggest that these interactions in crystalline dcc help to 'polymerise' the corrinoid molecules and to promote the formation of well developed crystals in this particular 'cobester'. The occurrence of such an unusual type of interaction obviously requires unusual conditions, *viz.* the exclusion of both strong ionic interactions (dcc is uncharged) and H-bonds (a reason why only one cyanide is H-bonded is suggested below) and the provision of methyl groups with a slight positive charge (incorporated into the ester side-chains).

It has been pointed out[44] that steric factors prevent all side-chains except f and g (both on ring D) from being able to project out 'equatorially' from the corrin ring. Side-chain f always extends down, even when its freedom of movement is not restricted by forming part of the cobalamin side-chain. Side-chain g, on the other hand, always shows a bend which places an O (never a N) atom on the other side of the plane of the corrin ring (see Figure 3) in all but one of the *ca.* 20 corrinoid structures which have been reported, whether the side-chains are hydrophobic or hydrophilic; see refs. 44 (Figures 2—7), 45, and 46. In addition, Figure 13 of ref. 44 emphasises that the conformation of the whole of side-chain g shows less variation than that of any other side-chain, *i.e.* it shows an unusual and persistent conformation which is independent of H-bonding and packing factors and of the presence or absence of the nucleotide loop. The single exception is provided by vitamin B_{12} 5′-phosphate, in which the acetamide is rotated away from the 5′-phosphate region with O(62) undergoing the greatest displacement, compared to its position in vitamin B_{12};[47] this strongly suggests that the unusual conformation of side-chain g is governed by coulombic, not steric, factors. In both molecular dcc and, as far as can be judged from published diagrams,[44] in all other corrinoids the nearest contact of O(62) is with the methyl group C(20), which is situated in a very unusual environment [proximity to N(21), Co, and dbzm as well as O(62); very distorted bond angles around C(1)] and may therefore have unusual properties. We suggest that the methyl C(20) may carry a slight positive charge which promotes interaction with the negative dipole of O(62).

Table 3 shows that, where there is no change in the nature of the axial ligands, the spectra of all types of corrinoids are relatively insensitive to a change in the environment; the five-co-ordinate cyclohexylcorrinoids provide a 'blank' to test for the possible (in fact, negligible) effect of solvent directly on the corrin ring. One can therefore interpret the spectra shown by the vitamin B_{12}-dependent enzymes (especially the anomalous band at *ca.* 440 nm seen during the enzymatic reaction)[48] in terms of the spectra seen in aqueous solution. The apparently larger solvent effect shown by methylcorrinoids probably reflects the existence of mc as a mixture of products (see Experimental section and Results) and the marked difference between the two axial isomers in spectra[49] and, presumably, in their equilibria with the six-co-ordinate aqua complex.[29c] The solvent effect observed with the Co^I corrinoids may be due to a partial charge-transfer character in the transitions.[50] The solvent effect on the spectrum of dcc has been studied in more detail (see Table 4 and Figures 5—7); the effects of H-bonding are considered first.

The spectrophotometric titration of dcc in CCl_4 with MeOH showed the occurrence of two main equilibria; the first involves the binding of one MeOH per Co with an apparent $K_1 = 7$ $dm^3\ mol^{-1}$ and the occurrence of isosbestic points at several wavelengths, the second with $K_2 \leqslant 0.05$ $dm^3\ mol^{-1}$. The apparent values represent the resultant of (*a*) the rupture of MeOH ··· MeOH H-bonds and (*b*) reorganisation of the Co–CN unit as well as (*c*) formation of the CN ··· MeOH H-bond, and the additional interactions which break the isosbestic points at certain wavelengths could represent either (*i*) further H-bonding between the O atom of Co–CN ··· HOMe and other MeOH molecules and/or (*ii*) less specific interaction (*e.g.* with the π-electrons of CN) of the type reported for isocyanide complexes.[32] A significant reduction in K_2 compared to K_1 is expected on the basis of (*i*) the reduction in donor power of the cyanide on H-bonding (see below) and (*ii*) the known thermodynamic *trans* effect in corrinoids.[29e] This could explain why only one H-bond is formed in the solid state; the energy of forming the second H-bond has been reduced to such an extent that it is insufficient to overcome the adverse free energy of introducing a polar molecule into a hydrophobic environment. Hydrogen-bonding to cyanide in dcc is associated with a shift in λ_γ from *ca.* 374 nm (in CCl_4) to 369.9 nm (in *ca.* 20% MeOH) for one H-bond and to $\leqslant$368 nm (in H_2O) for two H-bonds; the direction of this shift corresponds, as expected,[29a] to a reduction in the donor power of the cyanide to the Co. Hydrogen bonding also increases the CN stretching frequency (from 2 117 cm^{-1} in CCl_4 to 2 123 cm^{-1} in the adduct with one H-bond), which parallels the effects of protic solvents on the Co^{III} and Fe^{III} hexacyanide complexes (see Introduction) and the effect of further co-ordination to the terminal N {*cf.* ν_{CN} at 2 135 ± 10 cm^{-1} in $[Co^{III}(NH_3)_5(CN)]^{2+}$ and at 2 190 ± 10 cm^{-1} when co-ordinated to Ag^I}.[51] Experimental evidence indicates that the lifetime of a H-bond to $[Co(CN)_6]^{3-}$ is short enough ($\leqslant 10^{-12}$ s) to cause a merging of the CN stretching vibrations with and without a H-bond;[11] our failure to observe two separate CN bands for dcc in 18% MeOH–CCl_4, where only one cyanide should be H-bonded, also suggests that the half-life of the H-bond to dcc is very short and that in solution both cyanides are equally able to form H-bonds.

Inspection of Figure 6 shows that protic solvents fall on one line (A) and aprotic solvents fall near a second line (B), *except* for $CHCl_3$, $MeCO_2Me$, and MeCN (linked by line C), which are obviously anomalous. In addition, the occurrence of crossover points in the changes in spectrum observed during the titration of dcc in acetone with MeCN suggests the occurrence of some fairly specific Co–CN ··· MeCN interaction. In the light of i.r. evidence for the formation of H-bonds by $CHCl_3$,[52] and *X*-ray evidence for Co–CN ··· MeOCO– interactions (this work) and for MeCN ··· MeCN interactions,[43] we conclude that co-ordinated cyanide can interact with methyl groups carrying a slight positive charge (as in MeCN and methyl esters) and that this interaction is qualitatively similar to, though weaker than, normal H-bonds and probably comparable to the H-bonds formed by $CHCl_3$. We suggest that line B in Figure 6 represents the general 'solvent' effect of changes in $E_T(30)$, while lines A and C can be considered as a single line, the difference between lines A/C and B representing any additional effect due to the formation of a more specific 'bond' (H-bond or Me-bond). One would expect the divergence between lines A/C and B to increase with an increase in the polarity of the solvent but the data are, unfortunately, insufficient to prove it.

Combining present and previously published results (see Introduction) shows (*i*) that the formation of specific H-bonds to co-ordinated cyanide can be detected in solution as well as in the solid state, (*ii*) that the formation of an H-bond can markedly affect the properties of the co-ordinated cyanide (i.r.), the Co ion (*d*–*d* transitions, ^{59}Co n.m.r.) and the ligands in both the *cis* position (wavelength of π–π transitions) and the *trans* position (apparent reduction in K_2), (*iii*) that all these changes correspond to the expected reduction in electron density on the cyanide and hence in its donor power to the Co, and (*iv*) that the observed 'solvent effects' may represent a graded series of effects ranging from minimum interaction in CCl_4 through interaction with methyl groups carrying a slight positive charge and weak H-bonds (*e.g.* to $CHCl_3$), to more normal H-bonds with alcohols and H_2O, with a corresponding increase in the energy of interaction and hence in the importance of specific interaction over more random interaction. Cyanide complexes, in particular those of Co^{III} provide the most extensive set of data on external effects (*i.e.* effects of changes in the outer co-ordination sphere) available for any ligand and demonstrate how H-bonding effects of the type discussed for haemoproteins (see Introduction) can be transmitted from one axial ligand to the other. The nature of the Co–CN bond and the relative importance of σ- and π-bonding in these effects will be discussed later.

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References

1 Part 27, S. M. Chemaly, E. A. Betterton, and J. M. Pratt, *J. Chem. Soc., Dalton Trans.*, 1987, 761.
2 J. Halpern and P. J. Maher, *J. Am. Chem. Soc.*, 1965, **87**, 5361.
3 R. A. Firth, H. A. O. Hill, J. M. Pratt, R. G. Thorp, and R. J. P. Williams, *J. Chem. Soc. A*, 1968, 2428.
4 T. Funabiki and K. Tarama, *Bull Chem. Soc. Jpn.*, 1972, **45**, 2945.
5 D. Dodd and M. D. Johnson, *J. Chem. Soc., Dalton Trans.*, 1973, 1218.
6 D. A. Baldwin, E. A. Betterton, and J. M. Pratt, *S. Afr. J. Chem.*, 1982, **35**, 173.
7 J. M. Pratt and R. G. Thorp, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 375.
8 R. Quinn, J. Mercer-Smith, J. N. Burstyn, and J. S. Valentine, *J. Am. Chem. Soc.*, 1984, **106**, 4136.
9 G. A. Tondreau and D. A. Sweigart, *Inorg. Chem.*, 1984, **23**, 1060.
10 D. R. Eaton, C. V. Rogerson, and A. C. Sandercock, *J. Phys. Chem.*, 1982, **86**, 1365.
11 D. R. Eaton and A. C. Sandercock, *J. Phys. Chem.*, 1982, **86**, 1371.
12 P. Laszlo and A. Stockis, *J. Am. Chem. Soc.*, 1980, **102**, 7818.
13 A. Delville, P. Laszlo, and A. Stockis, *J. Am. Chem. Soc.*, 1981, **103**, 5591.
14 D. R. Eaton, R. J. Buist, and C. V. Rogerson, *Can. J. Chem.*, 1983, **61**, 1524.
15 S. C. F. Au-Yeung and D. R. Eaton, *J. Magn. Reson.*, 1983, **52**, 351.
16 E. Ragg and G. R. Moore, *J. Inorg. Biochem.*, 1984, **21**, 253.
17 W. R. Mason, *J. Am. Chem. Soc.*, 1973, **95**, 3573.
18 J. Bierrum, A. W. Adamson, and O. Bostrup, *Acta Chem. Scand.*, 1956, **10**, 329.
19 A. A. Schilt, *J. Am. Chem. Soc.*, 1957, **79**, 5421.
20 A. A. Schilt, *J. Am. Chem. Soc.*, 1960, **82**, 3000.
21 N. K. Hamer and L. E. Orgel, *Nature* (*London*), 1961, **190**, 439.
22 M. F. A. Dove and J. G. Hallett, *J. Chem. Soc. A*, 1969, 1204.
23 G. N. La Mar, J. Del Gaudio, and J. S. Frye, *Biochim. Biophys. Acta*, 1977, **498**, 422.
24 Y. Murakami, Y. Hisaeda, and T. Ohno, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 2091.
25 Y. Murakami, Y. Aoyama, and S. Nakanishi, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 809.
26 Y. Murakami, Y. Aoyama, A. Nakano, T. Tada, and K. Fukuya, *J. Am. Chem. Soc.*, 1981, **103**, 3951.
27 J. A. Hill, J. M. Pratt, and R. J. P. Williams, *J. Chem. Soc.*, 1964, 5149.

28 J. H. Fendler, F. Nome, and H. C. van Woert, *J. Am. Chem. Soc.*, 1974, **96**, 6745.

29 J. M. Pratt, 'Inorganic Chemistry of Vitamin B_{12},' Academic Press, London, 1972, (*a*) ch. 5; (*b*) ch. 6; (*c*) ch. 8.

30 R. P. J. Cooney and J. R. Hall, *J. Inorg. Nucl. Chem.*, 1966, **28**, 1679.

31 C. Reichardt, 'Solvent effects in organic chemistry,' Verlag Chemie, Weinheim, 1979.

32 W. D. Horrocks and R. H. Mann, *Spectrochim. Acta*, 1963, **19**, 1375.

33 L. Werthemann, Abhandlung, Eidgenössischen Technischen Hochschule (ETH), Zürich, 1968.

34 K. Kamiya and O. Kennard, *J. Chem. Soc., Perkin Trans. 1*, 1982, 2279.

35 A. Fischli and J. J. Daly, *Helv. Chim. Acta*, 1980, **63**, 1628.

36 D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, 'Purification of Laboratory Chemicals,' 2nd edn., Pergamon Press, Oxford, 1981, p. 320.

37 S. M. Chemaly and J. M. Pratt, *J. Chem. Soc., Dalton Trans.*, 1980, 2259.

38 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.

39 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

40 J. M. Pratt, in 'B_{12},' ed. D. Dolphin, Wiley-Interscience, New York, 1982, vol. 1, p. 325.

41 B. Grüning, Dissertation, Technical Universiiy of Braunschweig, 1979.

42 U. Liddel and E. D. Becker, *Spectrochim. Acta*, 1957, **10**, 70.

43 M. J. Barrow, *Acta Crystallogr., Sect. B*, 1981, **37**, 2239.

44 J. P. Glusker, in 'B_{12},' ed. D. Dolphin, Wiley–Interscience, New York, 1982, vol. 1, p. 23.

45 R. Bieganowski and W. Friedrich, *Z. Naturforsch., Teil B*, 1980, **35**, 1335.

46 J. Kopf, K. von Deuten, R. Bieganowski, and W. Friedrich, *Z. Naturforsch., Teil C*, 1981, **36**, 506.

47 S. W. Hawkinson, C. L. Coulter, and M. L. Greaves, *Proc. R. Soc. London, Ser. A*, 1970, **318**, 143.

48 J. M. Pratt, *J. Mol. Catal.*, 1984, **23**, 187; *Chem. Soc. Rev.*, 1985, **14**, 161.

49 W. Friedrich and R. Messerschmidt, *Z. Naturforsch., Teil B*, 1969, **24**, 465.

50 S. M. Chemaly and J. M. Pratt, *J. Chem. Soc., Dalton Trans.*, 1984, 595.

51 H. Siebert, *Z. Anorg. Allg. Chem.*, 1964, **327**, 63.

52 R. Massuda and C. Sandorfy, *Can. J. Chem.*, 1977, **55**, 3211.

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