The Chemistry of Vitamin B_{12}. Part 26.[1] Co-ordination of the Malonitrile Anion by Co^{III} Corrinoids: First Experimental Determination of Equilibrium Constants for the Co-ordination of a Tetrahedral Carbanion by a Transition–metal Ion

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Equilibrium constants for the substitution of co-ordinated H_2O by the malonitrile anion, $CH(CN)_2^-$, in the Co^{III} corrinoids aquocobalamin and diaquocobinamide have been determined in aqueous solution at 25 °C as log K ($dm^3 mol^{-1}$) = 7.4 and *ca.* 11.5 respectively.

All the known B_{12}-dependent enzymatic reactions involve the making and breaking of a σ Co^{III}–C bond.[2a–i] For general reviews on the making and breaking of Co–C bonds in the Co corrinoids see refs. 2*j*—*n*; here we wish to focus attention on the thermodynamic aspects of the heterolysis of such bonds to give the hydrocarbon. It has been widely assumed that the stability of the hydrido-complexes and of the corresponding organo-complexes is mainly due to the total ligand-field stabilisation energy of the ligands in the complex, so preventing dissociation to produce the reactive entities H^- and R^-, which would be immediately destroyed by air or moisture,[3] *i.e.* that M–H and σ M–C bonds involving transition-metal ions are thermodynamically unstable towards hydrolysis by H_2O to give H_2 and RH (together with the aquo- or hydroxo-complex). We have, however, shown that this is incorrect at least in the case of two Co^{III}–H bonds; the equilibrium constant for the substitution of co-ordinated H_2O by H^- has values of log $K \geqslant 29$ and 41 in $[Co(CN)_5(OH_2)]^{2-}$ and dac† respectively,[4,5] based on a pK of 35 for H_2.[6] No equilibrium constants have yet been reported for the co-ordination of any tetrahedral carbanion by a transition-metal ion, although several such constants have recently been determined for the $[HgMe]^+$ cation in aqueous solution.[7] It has also been found that certain Co^{III} complexes containing a conjugated equatorial ligand such as salen, $(Hdmg)_2$, porphyrin and even corrin can form a σ Co–C bond by reaction in non-aqueous or aqueous alcoholic solution with compounds possessing an acidic proton such as malonitrile $[CH_2(CN)_2]$, nitromethane (CH_3NO_2), or acetone (CH_3COCH_3).[8–16] Structures have been determined by *X*-ray analysis for complexes with Co–CH_2CN,[9] Co–$CH(CN)_2$,[10,12] Co–CH_2COCH_3,[9,14] and Co–CH_2NO_2 bonds.[16] Amongst the corrinoids the only examples so far reported involve the reaction of aquocobalamin (B_{12a}) when left overnight with $CH_2(CN)_2$ or $PhCH_2CN$ in 50% aqueous methanol;[13] the products show spectra which indicate the presence of alkylcobalamins, but neither the stoicheiometry nor the equilibrium constant of the reactions was determined. We report here the determination, by u.v.–visible spectrophotometry, of equilibrium constants for the substitution of co-ordinated H_2O by $CH(CN)_2^-$ in dac and B_{12a}, together with qualitative studies on the co-ordination of $CH_2NO_2^-$. The following pK's have been used: dac, pK_1 5.9;[17] B_{12a}, pK 7.8;[18a] $CH_2(CN)_2$, pK_a 11.2;[19] CH_3NO_2, pK_a 10.2.[19]

Experimental

Materials.—Samples of B_{12} and B_{12a} were kindly given by Mr. A. P. Domleo of Glaxo-Allenbury (Pty) Ltd. Cyanoaquo-[20] and diaquo-cobinamide[17] were prepared as previously described. $CH_2(CN)_2$ and CH_3NO_2 (both Merck) were redistilled under reduced pressure (*ca.* 20 mmHg) before use and stored at 5 °C.

Methods.—U.v.—visible spectra were recorded with a JASCO UVIDEC-1 spectrophotometer using 1-cm cells thermostatted at 25 °C. The concentrations of the corrinoids were determined after conversion to the dicyanide, using molar $A_{367} = 3.04 \times 10^4$.[18b] A Metrohm EA 147 microglass electrode was used for pH determinations. Sodium phosphate buffers with I = 0.2 mol dm^{-3} were used for pH 5.00, 5.93, and 6.00 and 0.01 mol dm^{-3} NaO_2CMe with 0.19 mol dm^{-3} $NaClO_4$ for pH 3.91.

Results

Preliminary Results on the Co-ordination of Malonitrile.—Initial experiments showed that B_{12a} and dac both reacted readily with $CH_2(CN)_2$ in approximately neutral solution, provided that the reagent was present in a large excess, and with isosbestic points to give two new complexes (**1**) and (**2**), which are identified as the corrinoids possessing the axial ligands dbzm–Co–$CH(CN)_2$ and H_2O–Co–$CH(CN)_2$ respectively. Their spectra (see Figure 1) are characterised by bands at the following wavelengths (in nm) with molar absorption coefficients (× 10^{-4} $dm^3 mol^{-1} cm^{-1}$) given in parentheses: (**1**) α 560 (sh), β 527 (0.8), 426, 409, γ 369 (1.9), 355, 333, and 314; (**2**) α ~ 535 (sh), β 501 (0.9), 423, 406, γ 354 (2.1), and 337 (1.8). As expected for a cobalamin with a Co–C bond,[18c] (**1**) was found to be light-sensitive (decomposes on standing in air-saturated solution in daylight to give B_{12a}) and to undergo a reversible change on acidification to give a spectrum similar or identical to that of (**2**) [bands at ~540 (α), 502 (β), 353 (γ), and 338 nm], which can be ascribed[18d] to the protonation of dbzm with simultaneous displacement from co-ordination. Cyanoaquocobinamide also reacts with $CH_2(CN)_2$, but the spectrum indicates the formation of a mixture of the dicyanide (bands at 367, 540, and 580 nm) and (**2**), with no additional bands (*e.g.* beyond 580 nm) which could be ascribed to any NC–Co–$CH(CN)_2$ complex; the reaction can therefore probably be written as in equation (1). Studies with $CH_2(CN)_2$ at pH ≥ 7

$$2\,NC{-}Co{-}OH_2 + CH_2(CN)_2 \longrightarrow NC{-}Co{-}CN + H_2O{-}Co{-}CH(CN)_2 + H^+ \quad (1)$$

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† Abbreviations: dac = diaquo- and/or aquohydroxo-cobinamide, depending on the pH; B_{12a} = aquo- and/or hydroxo-cobalamin, depending on the pH; dbzm = the heterocyclic base (5,6-dimethylbenzimidazole) present in the cobalamin side-chain; Hdmg = dimethylglyoximate(1−) monobasic anion; salen = *NN'*-ethylenebis(salicylideneiminate); R = alkyl ligands and radicals. N.B. The cobinamides lack the nucleotide side-chain ending in dbzm, which is present in the cobalamins such as cyanocobalamin (B_{12} itself).

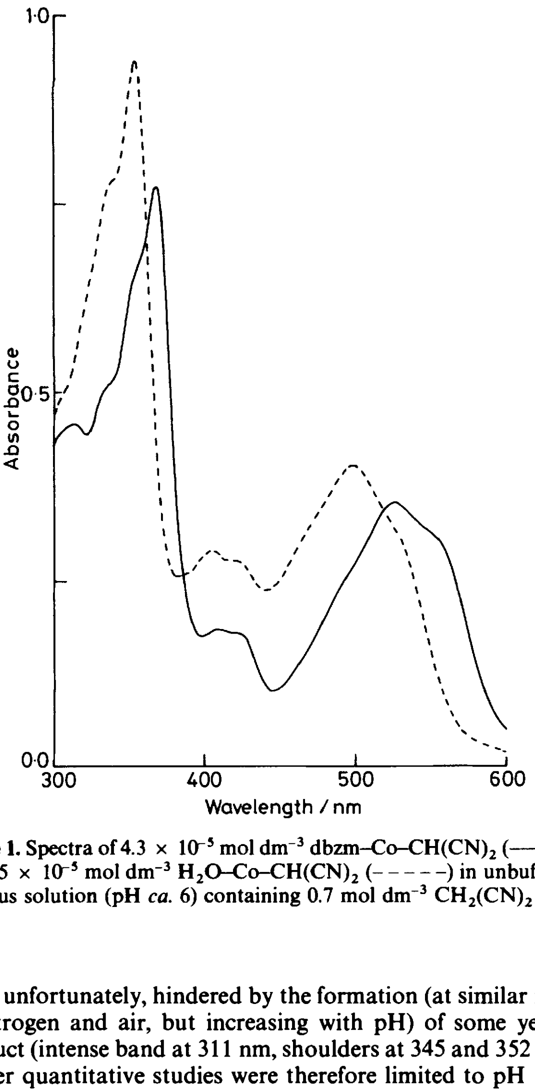

Figure 1. Spectra of 4.3×10^{-5} mol dm^{-3} dbzm–Co–$CH(CN)_2$ (———) and 4.5×10^{-5} mol dm^{-3} H_2O–Co–$CH(CN)_2$ (- - - - -) in unbuffered aqueous solution (pH *ca.* 6) containing 0.7 mol dm^{-3} $CH_2(CN)_2$

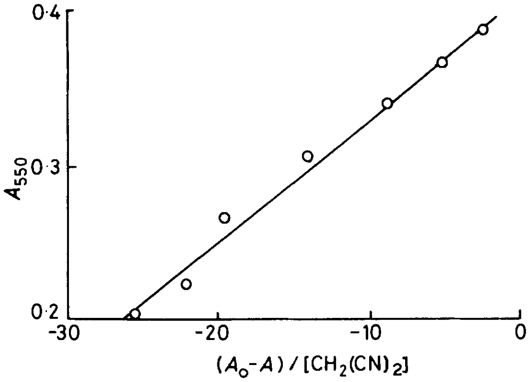

Figure 2. Evaluation of the experimental data for the equilibrium between B_{12a} and $CH_2(CN)_2$ at pH 5.93 to give a slope ($= 1/K_{app}$) of 7.96×10^{-3} mol dm^{-3}

were, unfortunately, hindered by the formation (at similar rates in nitrogen and air, but increasing with pH) of some yellow product (intense band at 311 nm, shoulders at 345 and 352 nm); further quantitative studies were therefore limited to pH < 7. Solid samples of (**1**) can be prepared by allowing unbuffered aqueous solutions of B_{12a} and $CH_2(CN)_2$ (*e.g.* 10% by volume) to equilibrate in the dark for 1 h. Extraction with diethyl ether and evaporating off the solvent leaves a red solid which, on dissolution in water, regenerates the spectrum of (**1**) but slowly dissociates back to B_{12a}. The i.r. spectrum (KCl disc) of (**1**) shows only a single band in the CN stretching region at 2 220 cm^{-1}.

Determination of Equilibrium Constants involving Malononitrile.—The apparent equilibrium constant K_{app} [defined by equation (2) where X can be dbzm or H_2O and R^- can be

$$K_{app} = \frac{[X\text{–Co–}R]}{([X\text{–Co–}OH_2] + [X\text{–Co–}OH])([R^-] + [HR])} \quad (2)$$

$CH(CN)_2^-$ or $CH_2NO_2^-$] for the co-ordination of $CH(CN)_2^-$ by B_{12a} at pH 5.93 was determined both directly under equilibrium conditions and indirectly from the ratio of the forward and reverse rate constants. A 4.7×10^{-5} mol dm^{-3} solution of B_{12a} in pH 5.93 buffer at 25 °C was titrated with a 1.80 mol dm^{-3} aqueous solution of $CH_2(CN)_2$, allowing sufficient time (*ca.* 1 h) for equilibration after each addition. Superposition of the final equilibrated spectra gave isosbestic points with no evidence for any species in addition to (**1**) and B_{12a}; analysis of the values of A_{550} (see Figure 2) by the method of Newton and Arcand[21] showed that the equilibrium involved one $CH_2(CN)_2/CH(CN)_2^-$ per Co with $K_{app} = 1.26 \times 10^2$ dm^3 mol^{-1}.

The rate of formation of (**1**) was studied with 5.1×10^{-5} mol dm^{-3} B_{12a} and variable $CH_2(CN)_2$ concentration and pH; isosbestic points were observed. Evaluation of the changes in A_{560} showed that the reactions followed first-order kinetics for over three half-lives to give the following pseudo-first-order rate constants: (*a*) pH 5.93 with (*i*) 4.5×10^{-2} mol dm^{-3} $CH_2(CN)_2$, 2.4×10^{-3} s^{-1}, (*ii*) 0.18 mol dm^{-3} $CH_2(CN)_2$, 9.6×10^{-3} s^{-1}, and (*iii*) 0.44 mol dm^{-3} $CH_2(CN)_2$, 2.6×10^{-2} s^{-1}; (*b*) pH 5.00, with 0.44 mol dm^{-3} $CH_2(CN)_2$, 7.5×10^{-3} s^{-1}. The results show that the rate constants increase with both $CH_2(CN)_2$ concentration and pH, as expected for a reaction with the conjugate base $CH(CN)_2^-$; the average of the three readings at pH 5.93 gives an apparent (*i.e.* pH-dependent) second-order rate constant of 0.055 dm^3 mol^{-1} s^{-1}. If we assume that the conjugate acid [$CH_2(CN)_2$] is kinetically inert, then correction for the pK_a of $CH_2(CN)_2$ (11.2)[19] gives a true second-order rate constant for the reaction of aquocobalamin with $CH(CN)_2^-$ of 1.0×10^4 dm^3 mol^{-1} s^{-1}.

The reverse decomposition of 6.7×10^{-5} mol dm^{-3} solutions of (**1**) [prepared as described above in the absence of excess $CH_2(CN)_2$] to B_{12a} also showed isosbestic points and followed first-order kinetics [evaluated from A_{369}, with the end-point established by photolysis of undecomposed (**1**)] for over three half-lives to give rate constants which were virtually independent of pH, *viz.* 3.6×10^{-4} s^{-1} at pH 5.93 and 3.9×10^{-4} s^{-1} at pH 3.91. The value of the ratio $k_f/k_r = 0.055/(3.9 \times 10^{-4}) = 1.4 \times 10^2$ dm^3 mol^{-1} at pH 5.93 then yields an independent value for K_{app} for the reaction of B_{12a} with $CH_2(CN)_2$ at this pH.

The pK for the protonation and displacement of dbzm in (**1**) was determined by injecting 50 µl of a concentrated, freshly prepared solution of (**1**) into 2-cm^3 solutions of Na/$HClO_4$ of varying pH (−0.8 to 3.9) but fixed ionic strength (I = 0.2 mol dm^{-3}) (except for the most acidic) and containing 0.2 mol dm^{-3} $CH_2(CN)_2$ in order to reduce the rate of dissociation. Values of A_{369} were recorded within 10 s of mixing and no significant changes were observed over the next 30 s, *i.e.* the values represent equilibrium values. Analysis of the data gave pK = 1.6 ± 0.1 involving 1.0 proton.

Attempts were made to determine K_{app} for the co-ordination of $CH(CN)_2^-$ by dac under equilibrium conditions at pH 6.0, but the rate of reaction with the required low concentrations of $CH_2(CN)_2$ was so slow that only a minimum value of log $K_{app} \geqslant 4.3$ could be obtained. The same equilibrium constant can, however, be obtained indirectly from the pK of (**1**) (see Discussion section).

Observations on the Co-ordination of Nitromethane.—Quantitative and detailed studies on the co-ordination of CH_3NO_2 by corrinoids were not attempted because the important γ-band region of the corrinoids was obscured by the absorption due to CH_3NO_2 (starting at *ca.* 400 nm). Preliminary experiments established that dac reacts readily with CH_3NO_2 at pH 6 to give a new complex (**3**) which, by analogy with the reaction of $CH_2(CN)_2$, can fairly confidently be assigned the structure $H_2O\text{–}Co\text{–}CH_2NO_2$, and that $\log K_{app} > 1.6$. Its spectrum shows bands at 525 (sh), 492 (max), 426, and 406 nm.

Discussion

The product (**1**) from the reaction of $CH_2(CN)_2$ with B_{12a} can be identified as malonitrilatocobalamin with the axial ligands $dbzm\text{–}Co\text{–}CH(CN)_2$ from (*a*) the stoicheiometry of the equilibrium constant [one $CH_2(CN)_2$ per Co], (*b*) the pH dependence of the rate of formation and the pH independence of the rate of dissociation [hence the ligand is the conjugate base $CH(CN)_2^-$], and (*c*) the CN stretching frequency of 2 220 cm^{-1} [all known $Co\text{–}CH(CN)_2$ complexes show a band in the region 2 215—2 228 cm^{-1}].[11,14] The product (**2**) from the reaction of $CH_2(CN)_2$ with dac can be identified as the analogous cobinamide with the axial ligands $H_2O\text{–}Co\text{–}CH(CN)_2$ from (*a*) the stoicheiometry of the protonation of (**1**), and (*b*) the similarity between the spectra of (**2**) and acidified (**1**); the existence of isomers involving inversion of the axial ligands (as in the case of $H_2O\text{–}Co\text{–}CN$ and $H_2O\text{–}Co\text{–}C{\equiv}CH$)[22] seems likely but has not been investigated. The value of p*K* = 1.6 for the protonation and displacement of dbzm in (**1**) is similar to the values reported for cobalamins with the ligands CF_3^- (p*K* 1.44)[23] and $CH_2CO_2H^-$ (1.50);[18e] this suggests that all these carbanions have a similar σ-donor power, which is intermediate between that of $HC{\equiv}C\text{–}$ (0.7) and $CH_2{=}CH\text{–}$ (2.4).[18e]

Very similar values of 1.26×10^2 and 1.4×10^2 $dm^3\ mol^{-1}$ (*i.e.* $\log K_{app} = 2.1$) were obtained for the apparent equilibrium constant for the co-ordination of $CH(CN)_2^-$ by B_{12a} at pH 5.93 by both the direct (equilibrium) and indirect (kinetic) methods. Correction for the p*K* of $CH_2(CN)_2$ (11.2)[19] then gives a value for the true equilibrium constant, $K_1 = [dbzm\text{–}Co\text{–}CH(CN)_2]/[dbzm\text{–}Co\text{–}OH_2][CH(CN)_2^-]$ or $\log K_1 = \log K_{app} + pK_a - pH = 2.1 + 11.2 - 5.9 = 7.4$. Only a minimum value of $\log K_{app} \geqslant 4.3$ could be obtained for the analogous equilibrium involving $CH_2(CN)_2$ and dac at pH 6.0 which, after correction for the p*K*'s of dac (5.9)[17] and $CH_2(CN)_2$ (11.2),[19] gives $\log K_2 \geqslant 10$, where $K_2 = [H_2O\text{–}Co\text{–}CH(CN)_2]/[H_2O\text{–}Co\text{–}OH_2][CH(CN)_2^-]$. A value for K_2 can, however, also be obtained by the use of equation (3) in the form $\log K_2 = \log K_3 + \log K_1 - \log K_4$, where K_3 and K_4 are the equilibrium constants for the displacement of co-ordinated H_2O by the unprotonated dbzm in the cobalamin side-chain when the *trans*-ligand X is H_2O and $CH(CN)_2^-$ respectively. Since $\log K_3 = pK'' - pK_3$ and $\log K_4 = pK'' - pK_4$, where pK'' is the p*K* for the protonation of dbzm when unco-ordinated (but still part of the cobalamin side-chain) and pK_3 and pK_4 are the p*K*'s for the protonation and displacement of dbzm from co-ordination in B_{12a} and (**1**) respectively, $\log K_2 = \log K_1 + pK_4 - pK_3$. Very similar values have been determined for pK'' in the 1- (or α-) isomer of methylcobalamin, where the methyl ligand occupies the lower site and dbzm is sterically unable to co-ordinate (4.8),[24] in dicyanocobalamin (5.0),[25] and in various alkylcobalamins (4.9—5.0);[26] pK'' appears to be independent of the nature of the axial ligands with a value of 4.9 ± 0.1. A value of $pK_3 = -2.4 \pm 0.2$ was obtained by u.v.–visible spectrophotometry of solutions of B_{12a} in $H_2O\text{–}H_2SO_4$ mixtures using the Hammett acidity function H_0.[27] This value was confirmed by the good agreement between the values of E^0 for the $Co^{II/III}$ couple determined for two corrinoids with identical axial ligands ($H_2O\text{–}Co\text{–}OH_2$) but different side-chains, *viz.* (*i*) dac at pH ⩾ 0 where $E^0 = 0.26$ V *vs.* saturated calomel electrode (s.c.e.) and (*ii*) B_{12a} at pH < 0, where a value of $E^0 = 0.27$ V *vs.* s.c.e. can be calculated from the experimental data if one *assumes* that $pK_3 = -2.4$;[28] this agreement also suggests that the values of E^0 and pK_3 are not significantly affected by protonation of either the phosphoric acid ester ($pK_1 + 0.3$)[29] or any of the amide side-chains. The value of $pK_4 = 1.6 \pm 0.1$ has been determined in this paper. We can therefore calculate that $\log K_2 = \log K_1 + pK_4 - pK_3 = 7.4 + 1.6\ (\pm 0.1) + 2.4\ (+0.2) = 11.4 \pm 0.3$, *i.e. ca.* 11.5. As expected from previous studies of the thermodynamic *trans*-effect,[18d] the binding constant is greater for dac than B_{12a}.

$$K_2 = \frac{[H_2O\text{–}Co\text{–}CH(CN)_2]}{[H_2O\text{–}Co\text{–}OH_2][CH(CN)_2^-]} = \frac{[dbzm\text{–}Co\text{–}OH_2]}{[H_2O\text{–}Co\text{–}OH_2]} \cdot \frac{[dbzm\text{–}Co\text{–}CH(CN)_2]}{[dbzm\text{–}Co\text{–}OH_2][CH(CN)_2^-]} \cdot \frac{[H_2O\text{–}Co\text{–}CH(CN)_2]}{[dbzm\text{–}Co\text{–}CH(CN)_2]} = K_3 \cdot K_1 \cdot \frac{1}{K_4} \quad (3)$$

Correcting the minimum value of $\log K_{app} > 1.6$, for the co-ordination of CH_2NO_2 at pH 6, for the p*K* (10.2)[19] of CH_3NO_2 gives $\log K_1 \geqslant 6$ for the substitution of co-ordinated H_2O by $CH_2NO_2^-$ in dac.*

Our results show that the Co^{III} ion is able to form σ Co–C bonds to at least two ligands with tetrahedral C atoms [$CH(CN)_2^-$ and $CH_2NO_2^-$], which, like the Co–H bonds, are thermodynamically stable towards hydrolysis; the same probably applies to most or all of the Co^{III}–carbanion complexes with electronegative substituents (see Introduction section) which were first reported by Costa and McKenzie and their co-workers in 1970—1971.[8–10] The remarkable stability of the Co^{III}–C bonds is further emphasised by the cyanide complexes. A value of $\log K_1' = 14.1$ [the constants K_n' involving CN^- are analogous to the constants K_n involving $CH(CN)_2^-$] has been determined for the co-ordination of CN^- by B_{12a};[30] together with the value of $pK_4' = +0.1$,[27] this can be used to obtain the value of $\log K_2' = \log K_1' + pK_4' - pK_3 = 14.1 + 0.1 + 2.4 = 16.6$ for the substitution of co-ordinated H_2O in dac by cyanide.

Our values of $\log K$ ($dm^3\ mol^{-1}$) = 7.4 and *ca.* 11.5 for the substitution of co-ordinated H_2O by $CH(CN)_2^-$ in B_{12a} and dac respectively appear to be the first equilibrium constants reported for the co-ordination of any tetrahedral carbanion by any transition-metal ion. Comparison with the values of $\log K = 14.1$[31] and 10.4[7] reported for the co-ordination of CN^- and $CH(CN)_2^-$ respectively by the $[HgMe]^+$ cation demonstrates that the Co^{III} ion in B_{12a} and dac and the Hg^{II} ion in $[HgMe]^+$ have similar affinities for these carbanions. Possible reasons for the unusual stability of Co^{III}–H and σ Co^{III}–C bonds, and hence for the choice of B_{12} as the co-factor for enzymatic organometallic chemistry, have been discussed.[21]

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* A referee considers that this complex may have the structure $Co\text{–}CH{=}NO(OH)$.

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References

1 Part 25, D. A. Baldwin, E. A. Betterton, S. M. Chemaly, and J. M. Pratt, preceding paper.

2 D. Dolphin, (ed.), 'B_{12},' Wiley, New York, 1982, chapters by (*a*) J. M. Wood, vol. 2, p. 151; (*b*) L. G. Ljungdahl and H. G. Wood, vol. 2, p. 165; (*c*) J. J. Barker and T. C. Stadtman, vol. 2, p. 203; (*d*) T. Toraya and S. Fukui, vol. 2, p. 233; (*e*) B. M. Babior, vol. 2, p. 263; (*f*) R. L. Switzer, vol. 2, p. 289; (*g*) R. T. Taylor, vol. 2, p. 307; (*h*) J. Rétey, vol. 2, p. 357; (*i*) R. L. Blakley, vol. 2, p. 381; (*j*) K. L. Brown, vol. 1, p. 245; (*k*) H. P. C. Hogenkamp, vol. 1, p. 295; (*l*) J. M. Pratt, vol. 1, p. 325; (*m*) J. Halpern, vol. 1, p. 501; and (*n*) B. T. Golding, vol. 1, p. 543.

3 J. Chatt, *Proc. Chem. Soc.*, 1962, 318.

4 M. B. Mooiman and J. M. Pratt, *S. Afr. J. Chem.*, 1982, **35**, 171.

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

6 E. Buncel and B. Menon, *J. Am. Chem. Soc.*, 1977, **99**, 4457.

7 J. M. T. Raycheba and G. Geier, *Inorg. Chem.*, 1979, **18**, 2486.

8 A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani, and G. Tauzher, *Inorg. Chim. Acta Rev.*, 1970, **4**, 41.

9 M. Cesari, C. Neri, G. Perego, E. Perrotti, and A. Zazzetta, *Chem. Commun.*, 1970, 276.

10 N. A. Bailey, B. M. Higson, and E. D. McKenzie, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 591.

11 D. Cummins, B. M. Higson, and E. D. McKenzie, *J. Chem. Soc., Dalton Trans.*, 1973, 414.

12 N. A. Bailey, B. M. Higson, and E. D. McKenzie, *J. Chem. Soc., Dalton Trans.*, 1975, 1105.

13 D. Cummins and E. D. McKenzie, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 521.

14 M. E. Kastner and W. R. Scheidt, *J. Organomet. Chem.*, 1978, **157**, 109.

15 W. Beck, T. Kemmerich, and H. Z. Böhme, *Z. Naturforsch., Teil. B*, 1979, **34**, 200.

16 L. Randaccio, N. Bresciani-Pahor, P. J. Toscano, and L. G. Marzilli, *Inorg. Chem.*, 1981, **20**, 2722.

17 D. A. Baldwin, E. A. Betterton, and J. M. Pratt, *J. Chem. Soc., Dalton Trans.*, 1983, 217.

18 J. M. Pratt, 'Inorganic Chemistry of Vitamin B_{12},' Academic Press, London, 1972, (*a*) p. 140, (*b*) p. 46, (*c*) ch. 14, (*d*) ch. 8, (*e*) pp. 142—143.

19 J. R. Jones, 'The Ionisation of Carbon Acids,' Academic Press, London, 1973.

20 R. A. Firth, H. A. O. Hill, B. E. Mann, J. M. Pratt, R. G. Thorp, and R. J. P. Williams, *J. Chem. Soc. A*, 1968, 2419.

21 T. W. Newton and G. M. Arcand, *J. Am. Chem. Soc.*, 1953, **75**, 2449.

22 D. A. Baldwin, E. A. Betterton, and J. M. Pratt, *J. Chem. Soc., Dalton Trans.*, 1983, 225.

23 K. L. Brown, J. M. Hakimi, D. M. Nuss, Y. D. Montejano, and D. W. Jacobsen, *Inorg. Chem.*, 1984, **23**, 1463.

24 M. Moskophidis, C. M. Klotz, and W. Friedrich, *Z. Naturforsch., Teil. C*, 1976, **31**, 255.

25 W. W. Reenstra and W. P. Jencks, *J. Am. Chem. Soc.*, 1979, **101**, 5780.

26 S. M. Chemaly and J. M. Pratt, *J. Chem. Soc., Dalton Trans.*, 1980, 2267.

27 G. C. Hayward, H. A. O. Hill, J. M. Pratt, N. J. Vanston, and R. J. P. Williams, *J. Chem. Soc.*, 1965, 6485.

28 N. R. de Tacconi, D. Lexa, and J. M. Savéant, *J. Am. Chem. Soc.*, 1979, **101**, 467.

29 K. L. Brown and J. M. Hakimi, *Inorg. Chim. Acta*, 1982, **67**, L29.

30 D. Lexa, J. M. Savéant, and J. Zickler, *J. Am. Chem. Soc.*, 1980, **102**, 2654.

31 G. Schwarzenbach and M. Schellenberg, *Helv. Chim. Acta*, 1965, **48**, 28.

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