# Cobalt(I) Tetradehydrocorrin Complexes

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The presence of *meso*-electron attracting groups such as cyano or nitro in cobalt tetradehydrocorrin complexes stabilises the metal in the cobalt(I) state, and with two or more such substituents the complexes can be isolated as stable solids. The cobalt(I) *meso*-cyano-complexes are produced by thermolysis of the dicyanocobalt(III) compounds and their structures have been confirmed by electrochemical studies.

ALTHOUGH there are many similarities between the chemistry of nickel(II) and cobalt(II) complexes, the ready interconversion of the various oxidation states of cobalt contrasts with the stability of divalent nickel, and marked variation in chemical behaviour may be encountered. This is well illustrated by the reactions of the cationic complexes of the 1,19-dimethyltetrade-hydrocorrins. We have already described [1] a number of substitution reactions of nickel(II) 8,12-diethyl-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrin salts (I; $R^1 = R^2 = H$) where the reactions occurred solely at the ligand. With the cobalt(II) analogues, we have now found that reactions may occur at the ligand as with the nickel salts. but more usually at the metal, involving a change in its oxidation state.

In the nickel series, the only substitution reactions which did not cause a simultaneous modification of the ring structure were chlorination and bromination, which gave unstable 5,15-dihalogeno-derivatives (I; $R^1 = R^2 = Cl$ or Br). These were identified by reaction with lithium dimethylcuprate to yield the 5,15-dimethyl derivative (I; $R^1 = R^2 = Me$). One of the most ready reactions of the nickel complex (I; $R^1 = R^2 = H$) was



(I)                              (II)
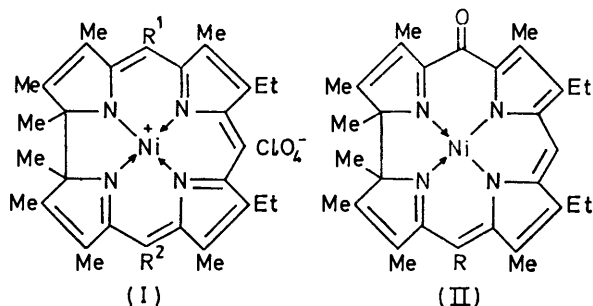
aerial oxidation in the presence of bases, when the product was the neutral keto-compound (II; R = H). Various derived products [*e.g.* (II; R = CHO, $NO_2$, or CN)] were formed in related reactions, although cyanation also gave two stable free radicals, the 5-cyano- and 5,15-dicyano-derivatives with the odd electron localised on the ligand.

The cobalt(II) tetradehydrocorrin salts are less stable than the nickel complexes; this is illustrated by their behaviour towards acids. The nickel macrocycles are relatively stable apart from undergoing anion exchange,

although with concentrated sulphuric acid, the metal is largely removed. On the other hand, the cobalt 1,19-dimethyltetradehydrocorrin salts are stable only in acids less than *ca.* 3N when anion exchange is again observed. The β-alkyl substituents stabilise the cobalt complexes towards acids and the β-unsubstituted cobalt(II) 1,19-dimethyltetradehydrocorrin salts are stable only in acid of <0·1N.[2] In more concentrated acids, *e.g.* 24% hydrobromic acid, the cobalt β-alkyl-ated macrocycles are readily cleaved forming yellow solutions which show an electronic spectrum typical of a monohydrobromide of a 1,19-dimethyl-1,19-dideoxybilatriene-*abc*. On separating the organic phase and washing with water, the organic phase became greener and then had the electronic spectrum of a bilatriene free base, which could be readily reconverted into the monohydrobromide with more acid.

For our study of the substitution reactions of the cobalt(II) tetradehydrocorrin salts we have used the 2,8,12,18-tetraethyl-1,3,7,13,17,19-hexamethyl perchlorate [3] (III). Treatment of the purple salt with cyanide gave a neutral green complex which was diamagnetic [4] and gave an electronic spectrum almost identical with that of the analogous compound prepared earlier [5] from cobalt(II) 8,12-diethyl-1,2,3,7,13,17,18,19-octamethyltetradehydrocorrin perchlorate (I; $R^1 = R^2 = H$, Co for Ni). The n.m.r. spectrum of the neutral green complex showed that three *meso*-protons were present and that there had been no addition or substitution of cyanide on the tetrapyrrolic ligand. Elemental analysis and the i.r. spectrum indicated the presence of two cyanide groups, which were therefore located in axial positions at the cobalt atom which had been oxidised to cobalt(III). The product was assigned the structure (IV); the mass spectrum showed the base peak at $m/e$ 552 ($M^+ - 2CN$).

Similarly, on shaking a solution of compound (III) with an excess of sodium azide a green colour was rapidly produced and the product was again diamagnetic (n.m.r. spectrum, although the resolution was poor). The i.r. spectrum and elemental analysis showed the presence of two azide groups, and the structure is analogous to (IV) ($N_3$ for CN). When the green azido-complex was kept on t.l.c. plates or in solution it

[1] A. Hamilton and A. W. Johnson, *J. Chem. Soc.* (C), 1971, 3879.
[2] A. W. Johnson and W. R. Overend, *J.C.S. Perkin I*, 1972, 2681.
[3] R. Grigg, A. W. Johnson, R. W. Kenyon, V. B. Math, and K. Richardson, *J. Chem. Soc.* (C), 1969, 176.
[4] Preliminary communication, A. Hamilton and A. W. Johnson, *Chem. Comm.*, 1972, 453.
[5] D. Dolphin, R. L. N. Harris, J. L. Huppatz, A. W. Johnson, and I. T. Kay, *J. Chem. Soc.* (C), 1966, 30.

decomposed to reform the original cobalt(II) complex, and, not unexpectedly, the mass spectrum of the green complex was identical with that of the starting product, indicating the loss of the axial azido-groups in the mass spectrometer. A similar neutral green complex was obtained from compound (III) with aqueous sodium nitrite and from the elemental analysis and spectra it was formulated as (IV; $NO_2$ or ONO for CN). Hydroxocobalamin reacts with sodium nitrite under similar conditions to give nitritocobalamin, the so-called vitamin $B_{12c}$.[6] It is clear that the neutral green cobalt(III) octahedral complexes are readily formed but the axial ligands are easily eliminated both in the mass spectrometer and by chemical means.

Thermolysis of the parent cobalt(II) 1,19-dimethyl-tetradehydrocorrin salts as in the nickel series [7] gave the analogous metal porphins. On the other hand, thermolysis of the green cobalt(III) dicyano-complex (IV) overnight at 100°, in degassed chlorobenzene, in an atmosphere of nitrogen gave a pink coloured solution. The pink thermolysis product, after it had been treated with 60% perchloric acid, was column chromatographed on Woelm grade IV basic alumina and eluted with methylene chloride. The first species to be eluted was pink and was a neutral product (6%). This compound, when treated with perchloric acid, gave a blue cobalt(II) salt which, from its spectral properties, analysis, and mass spectrum, is formulated as (IX). The salt was readily reconverted into the pink compound by t.l.c. on alumina (even to a slight extent on silica). This pink product was diamagnetic (n.m.r. spectrum), but because of its tendency to give the blue paramagnetic salt, resolution of the spectrum was poor. The mass spectrum (molecular ion, $m/e$ 602) and elemental analysis of the pink compound indicated the molecular formula $C_{35}H_{39}CoN_6$, i.e. corresponding to the parent macrocycle plus two cyanide groups. The electronic spectrum showed the band of the longest wavelength at 542 nm, and the i.r. spectrum showed a band at 2200 cm$^{-1}$ (C≡N). From the physical data the structure (VIII), a cobalt(I) complex, was proposed for this compound and further evidence to support this formulation will be presented later. The two cyanide groups were assigned to C-5 and C-15 mainly on n.m.r. evidence, i.e. the C-1 and C-19 angular methyl protons gave superimposable signals showing that the molecule had retained its ' North–South ' symmetry. The second band from the column gave the starting material (III), and the third band gave a purple, polar solid (43%) which showed an electronic spectrum typical of a cobalt 1,19-dimethyltetradehydrocorrin perchlorate with a bathochromic shift of ca. 18 nm of the band of the longest wavelength in the visible spectrum compared with that of the starting material (III). The mass spectrum (molecular ion, $m/e$ 576) and elemental analysis indicated the molecular formula $C_{34}H_{40}ClCoN_5O_4$, corresponding to the addition of one cyanide group, and this was

supported by the i.r. spectrum which showed a band at 2200 cm$^{-1}$ (C≡N). This salt was paramagnetic and hence was assigned the structure (VI). The assignment of the cyanide group to C-5 was deduced from the



Reagents: i, CN$^-$; ii, heat; iii, H$^+$; iv, OH$^-$; v, $Al_2O_3$; vi, $Ac_2O$–$Cu(NO_3)_2$; vii, MeOH–$Al_2O_3$
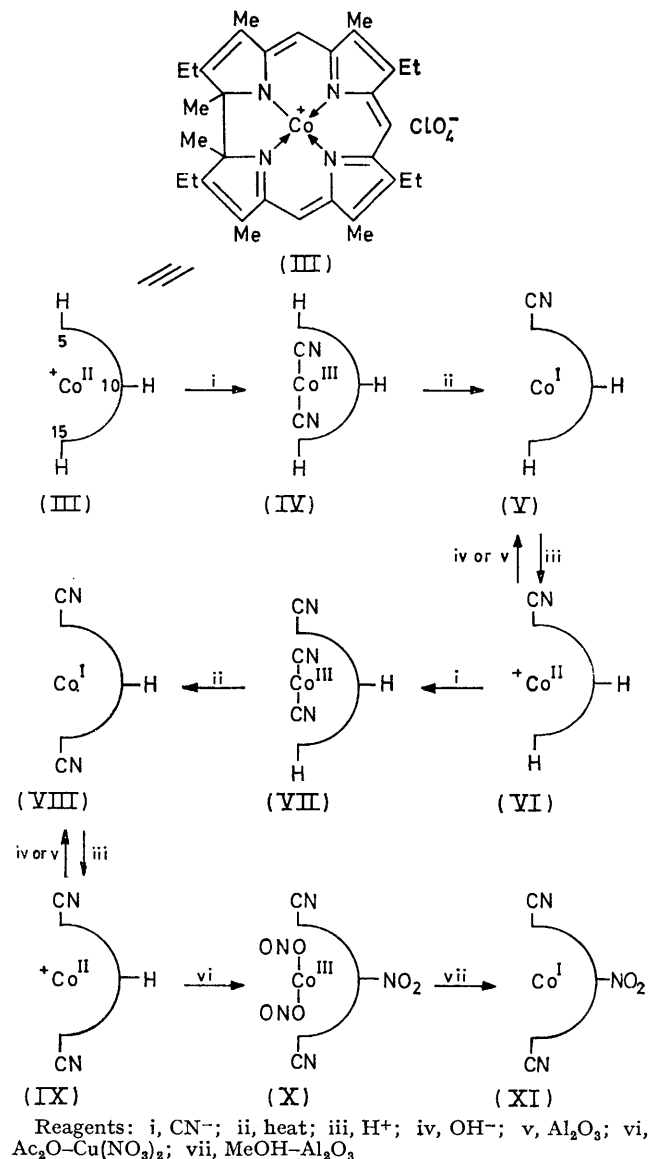
following conversion (42%) of (VI) into (IX) (where the cyanide substituents have already been assigned to positions C-5 and C-15). The monocyano-salt (VI) on further treatment with sodium cyanide reacted readily to give a green solution which was presumed to contain a cobalt(III) octahedral complex (VII). The mixture was diluted with water and saturated with sodium chloride. The mixture still appeared green but on extracting with methylene chloride at room temperature, the colour of the organic phase changed to pink. However, a better yield of a pink neutral compound (VIII), which was identical with that isolated

6 J. G. Buchanan, A. W. Johnson, J. A. Mills, and A. R. Todd, Chem. and Ind., 1950, 426.

7 R. Grigg, A. W. Johnson, K. Richardson, and K. W. Shelton, J. Chem. Soc. (C), 1969, 655.

previously, was produced by mild heating. The rearrangement of the cyano-groups from cobalt to carbon is probably intermolecular.

In the 5-monocyano-series, the pink neutral cobalt complex, although it could be formed in solution with base, or by t.l.c. on alumina, could not be isolated. However, when two electron-attracting cyano-*meso*-substituents were present the neutral cobalt(I) species formed readily, but was not very stable in solution. It seemed therefore that a 5,10,15-tri-*meso*-substituted derivative might be more stable. The 5,15-*meso*-dicyanocobalt(II) perchlorate (IX) was therefore dissolved in acetic anhydride and shaken with copper(II) nitrate in an attempt to nitrate the unsubstituted C-10 position. The mixture quickly turned green and when poured into methanol the product was converted into a purple salt. Concentration, dilution with an aqueous solution of sodium iodide, and extraction with methylene chloride caused the colour of the solution to change to pinkish purple, similar to that of the neutral cobalt(I) compounds already described. The product was converted completely into this neutral compound (52%) by t.l.c. on alumina, and then purified by further t.l.c. on silica. The new neutral compound was very stable and with acid it was not converted into a paramagnetic cobalt(II) salt. It was identified as (XI) on the following evidence. The mass spectrum (molecular ion, $m/e$ 647) and elemental analysis indicated a molecular formula $C_{35}H_{38}CoN_7O_2$. The electronic spectrum was similar to that of the neutral *meso*-dicyanocobalt(I) complex (VIII) and to that of the pink solution formed from treatment of the *meso*-monocyanocobalt(II) perchlorate (VI) with base. The n.m.r. spectrum showed no signals for *meso*-protons. The signals for the β-alkyl groups formed two groups: those for the C-1 and C-19 methyl groups were coincident indicating that the molecule possessed 'North–South' symmetry. Hence the cyano-substituents are located at C-5 and C-15 as in (XI).

Using conditions similar to those reported for the analogous nickel complex,[1] cobalt(II) 2,8,12,18-tetraethyl-1,3,7,13,17,19-hexamethyltetradehydrocorrin perchlorate (III) was dissolved in acetic anhydride and shaken with copper(II) nitrate. The colour of the reaction mixture changed from red through purple (*i.e.* probably indicating initial *meso*-nitration) to green and after 45 min the mixture was poured into methanol. The green colour changed to purple, and concentration, then dilution with a solution of aqueous sodium perchlorate, precipitated a purple salt. Examination of this purple solid by t.l.c. (SiO₂) showed that it consisted of a purple polar compound and a pink neutral compound. The purple polar compound isolated proved to be too involatile for a determination of its mass spectrum, but elemental analysis showed that it contained two nitro-groups in excess of the starting material. The compound was paramagnetic and its electronic spectrum was similar to that of the *meso*-dicyano-cobalt(II) perchlorate (IX). On t.l.c. on alumina, treatment with

base, or shaking with aqueous sodium iodide, the salt was readily converted into a pink neutral complex which had an electronic spectrum similar to that of the neutral *meso*-dicyanocobalt(I) complex (VIII). The molecular formula, $C_{33}H_{39}CoN_6O_4$, was determined from the mass spectrum (molecular ion, $m/e$ 642) and elemental analysis. The compound gave an n.m.r. spectrum, but the resolution was poor owing to transformation into the paramagnetic cobalt(II) complex. On this evidence the neutral product was formulated as either the 5,10- or the 5,15-dinitro-derivative of the cobalt(I) complex. The pink, neutral complex isolated from the nitration product by chromatography of the reaction mixture was purified by further chromatography in a less polar solvent system and crystallised to give the 5,10,15-trinitro-derivative of the cobalt(I) complex (16%), identified on the evidence of the mass spectrum (molecular ion, $m/e$ 687), and elemental analysis, which indicated a molecular formula $C_{33}H_{38}CoN_7O_6$; *i.e.* a trinitro-derivative. The electronic spectrum was similar to those of all the previous pink neutral complexes. This trisubstituted complex did not revert to a cobalt(II) salt on treatment with perchloric acid. The n.m.r. spectrum showed no remaining *meso*-protons and the C-1 and C-19 angular methyl group signals were superimposed (τ 9·14). An attempted nitration of the *meso*-dinitrocobalt perchloroate salt under conditions as described earlier gave a green solution, but on decomposition with methanol the *meso*-dinitro-salt was recovered unchanged. This suggests that two isomeric dinitro-derivatives, the 5,10- and 5,15-isomers were originally formed in the reaction mixture and one of these could be nitrated further to give the *meso*-trinitro-complex whereas the other could not.

The pink neutral complexes are diamagnetic and could therefore be cobalt(I), dimeric cobalt(II), or cobalt(III) complexes. In elemental analysis, colour (pink), and electronic spectra, they differed from the green cobalt(III) octahedral complexes of 1,19-dimethyltetradehydrocorrins, into which they could be transformed. Thus if the pink complexes are derivatives of cobalt(III) they must be neutral square planar cobalt(III) complexes. The difference between such structures and square planar cobalt(I) complexes is the oxidation states of the metal and ligand. In a



( VIII )          ( XII )
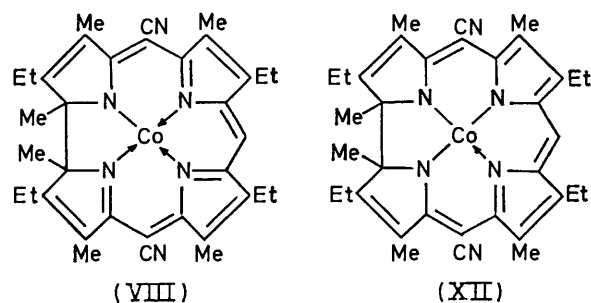
cobalt(III) complex (XII) there would be nine double bonds present, one of which is cross-conjugated, whereas in a cobalt(I) complex [*e.g.* (VIII)] there would be ten

double bonds, three of which are cross-conjugated, as in the *meso*-unsubstituted tetradehydrocorrin cobalt(II) salts. Hence it would be expected that the cobalt(I) complexes and the cobalt(II) salts, which have the same chromophore, should have similar electronic spectra, and this was found to be the case, with the band of the longest wavelength at *ca*. 500 nm.

Thus the choice of structure for the pink complexes seemed to rest between cobalt(I) [*e.g.* (VIII)] and dimeric cobalt(II) species, and as the stability of the series increased markedly with the number of electronegative substituents (*cf*. ref. 8) the cobalt(I) formulation seemed preferable. Molecular weight determinations (vapour phase osmometry) on the 5,15-dicyano-10-nitro-derivative showed that in dilute solution it existed as the monomer but that in more concentrated solutions, it tended to dimerise (*cf*. ref. 9). However, the most convincing evidence for the cobalt(I) formulation for these products came from polarographic and cyclic voltammetric studies; these results are summarised in the Table.

complexes were studied over the range $+0.3$ to $+0.7$ V and the voltammograms were found to exhibit an irreversible oxidation wave at $+0.54 \pm 0.02$ V at 90 mV s$^{-1}$ for all three complexes. The wave was assigned to the oxidation of cobalt(II) tetradehydrocorrin to cobalt(III).[13] The insensitivity of the oxidation potentials to the ring substituents can be attributed to the irreversibility of the electrode processes, which may obscure the effect of the substituents. In the case of the cobalt(I) trinitro- and dicyanomononitro-tetradehydrocorrins, cyclic voltammograms between 0.0 and $+0.4$ V indicated that the oxidation process was not completely reversible (difference between anodic and cathodic peak potentials *ca*. 100 mV).[10]

Polarograms of all the complexes with the exception of the dinitro- and trinitro-*meso*-substituted compounds gave well-defined reduction waves at negative potentials; *e.g.* for the reduction of the unsubstituted cobalt(II) tetradehydrocorrin a plot of electrode potential against the current function [log $(i/i_d - i)$],[14] where $i$ is the current flowing at the selected potential on the rising

Half-wave potentials of cobalt 2,8,12,18-tetraethyl-1,3,7,13,17,19-hexamethyltetradehydrocorrin complexes

| | $E_{\frac{1}{2}}/V$ [a] for reduction Co$^{II}$ $\xrightarrow{+e}$ Co$^{I}$ measured by: | | $E_{\frac{1}{2}}/V$ for reduction Co$^{I}$ $\xrightarrow{+e}$ Co$^{0}$ measured by polarography | $-\Delta E_{\frac{1}{2}}/V$ [b] ($E_{\frac{1}{2}}$ for Co$^{II}$ $\xrightarrow{+e}$ Co$^{I}$ minus $E_{\frac{1}{2}}$ for Co$^{I}$ $\xrightarrow{+e}$ Co$^{0}$) |
| *meso*-Substitution | Cyclic voltammetry [c] | Polarography | | |
| Unsubstituted | $-0.27$ | $-0.25$ | $-1.24$ | 0.99 |
| 5-Cyano | $-0.10$ | $-0.08$ | $-0.88$ | 0.80 |
| 5,15-Dicyano | $+0.09$ | | $-0.65$ | 0.74 |
| 5,15-(5,10?)Dinitro | $+0.07$ | | | |
| 5,15-Dicyano-10-nitro | $+0.31$ [d] | | $-0.52$ | 0.83 |
| 5,10,15-Trinitro | $+0.29$ [d] | | | |

[a] Potentials are quoted relative to a saturated aqueous calomel electrode.   [b] Where possible the appropriate polarographic values were used.   [c] Measurements on Pt electrode at 85·2% of peak current.[10]   [d] In the tri-*meso*-substituted species, the quoted figures refer to the oxidation potential for Co$^{I}$ $\xrightarrow{-e}$ Co$^{II}$.

Voltammograms between $+0.3$ and $-0.4$ V of the isolated *meso*-mono-, di-, and unsubstituted cobalt(II) salts met the criteria for a diffusion-controlled reversible one-electron reduction process. Typically, voltammograms of the reduction of the 5,15-dicyano-cobalt(II) complex (IX) exhibited a 60 mV difference between the peak and half-peak potentials;[10] analysis of the wave[11] indicated that for a one-electron process the transfer coefficient ($\alpha$) was 0·90 and, finally, the Malachesky factor[12] was 5·11, in good agreement with the theoretical value of 4·92 for a one-electron transfer. The unsubstituted salt was also examined in the mixed dichloromethane–methanol electrolyte and the $E_{\frac{1}{2}}$ value was found to be within 10 mV of the value determined in the methanol electrolyte. Furthermore, the *meso*-monocyano-, dicyano-, and unsubstituted

part of the wave and $i_d$ is the diffusion current measured on the plateau of the wave, was linear with a slope of 64 mV, indicating that the process involved one electron and was reversible. For polarograms where two reduction waves were observed the ratio of the wave heights was unity, suggesting that the second charge-transfer step also involved a single electron. The difference between the half-wave potentials (Table) is a measure of the free energy of the disproportionation process:

$$2Co^{I} \longrightarrow Co^{II} + Co^{0}$$

$$\text{where } \Delta G = -F\Delta E.$$
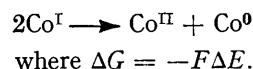
Since these disproportionation energies are an indication of the ground-state stabilities of the Co$^{I}$ complexes, then it is evident that substitution on the tetradehydrocorrin ring by electron-attracting groups stabilises the

[8] J. Bercaw, G. Guastalla, and J. Halpern, *Chem. Comm.*, 1971, 1594; J. Halpern and M. Pribanić, *J. Amer. Chem. Soc.*, 1971, **93**, 96; G. Guastalla, J. Halpern, and M. Pribanić, *ibid.*, 1972, **94**, 1574; N. E. Tokel, V. Katović, K. Farmery, L. B. Anderson, and D. H. Busch, *ibid.*, 1970, **92**, 700.

[9] Evidence for the association of metal prophins in solution: R. J. Abraham, P. A. Burbidge, A. H. Jackson, and D. B. MacDonald, *J. Chem. Soc.* (B), 1966, 620; D. A. Doughty and C. W. Dwiggins, *J. Phys. Chem.*, 1969, **73**, 423.

[10] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1964, **36**, 706.
[11] W. H. Reinmuth, *Analyt. Chem.*, 1961, **33**, 1793.
[12] P. A. Malachesky, *Analyt. Chem.*, 1969, **41**, 1493.
[13] A. Wolberg and J. Manassen, *J. Amer. Chem. Soc.*, 1970, **92**, 2982.
[14] L. Meites, ' Polarographic Techniques,' Interscience, New York, 2nd edn., 1965, p. 214.

$Co^I$ complexes relative to the unsubstituted one and that more than one substituent does not appear to increase the thermodynamic stability.

To confirm the reversibility of the cobalt(II)–(I) couple, controlled potential electrolyses were employed to prepare bulk samples of the reduced or oxidised forms of the cobalt tetradehydrocorrins, as appropriate. Attempts to form the unsubstituted and 5-monocyano-cobalt(I) complexes by reduction of the corresponding cobalt(II) salts did not reach completion presumably owing to the oxidation of the reduced cobalt by the solvent or by traces of water. However, electrolysis of the cobalt(II) 5,15-dicyano- and dinitro-substituted salts at 0·0 V proceeded to a negligible background current ($<100$ μA) and produced a stable cobalt(I) complex. The cobalt(I) dicyanotetradehydrocorrin formed by controlled potential reduction had the same half-wave potential and electronic spectrum as the isolated pink cobalt(I) dicyano-complex. Also the $E_{\frac{1}{2}}$ values of these reduced cobalt(I) complexes were within 10 mV of the values determined from the voltammo-grams of the corresponding cobalt(II) complexes. In the case of the tri-meso-substituted species, controlled potential oxidation of the dicyanomononitro-cobalt(I) complex produced a stable cobalt(II) species which displayed the same partially irreversible voltammetric behaviour as the parent cobalt(I) complex. By comparison, oxidation of the trinitro-cobalt(I) complex did not yield a stable cobalt(II) species.

The variation of the half-wave potentials of the cobalt(I) complexes clearly showed that they become more difficult to oxidise as the number of electron-withdrawing groups on the ligand increased, and the observed reversibility of the charge-transfer processes establishes that the cobalt(I) species are simple mono-meric complexes.

The mechanism of the effect of acids and bases on the oxidation states of cobalt in these complexes is controversial [15,16] although it finds a parallel in the reaction of base with the cobalt(III) complex, cyano-cobalamin (vitamin $B_{12}$) [17,18] which is reduced first to the cobalt(II) species, $B_{12r}$, and then to the cobalt(I) species, $B_{12s}$. In the $B_{12}$ series, the cobalt(I) derivative is unstable and is readily re-oxidised to the cobalt(III) complex, whereas in our compounds the cobalt(I) complexes are stabilised by the electronegative sub-stituents. $B_{12s}$ is claimed to form a five-co-ordinate complex with, for example, pyridine as the axial ligand,[19] although this is readily lost. In our series, treatment of the neutral cobalt(I) complexes with pyridine or triphenylphosphine caused no change in the electronic spectrum, but the meso-trisubstituted cobalt(I) dicyano-nitro- and trinitro-tetradehydrocorrins readily reacted

with 1 mol. equiv. of bromine to give green diamagnetic complexes each containing two bromine atoms. From their colour, electronic spectra, and elemental analysis they are postulated to be cobalt(III) octahedral complexes with two bromine atoms as the axial ligands. This provides further evidence for the formulation of the pink neutral compounds as cobalt(I) complexes rather than square-planar cobalt(III) complexes.

A comparison of the properties of the nickel(II) and cobalt(II) 1,19-dimethyltetradehydrocorrin salts thus reveals both similar and dissimilar features. The predominance of C-5 and C-15 substitition, as is also ob-served with the nickel(II) and cobalt(II) corrins,[20] is attributed to the maintenance of the longest conjugated system in the transition state. In the cobalt series the substitution reactions compete with reactions at the metal and in general the cobalt complexes are more reactive than the nickel complexes, as has been observed with the metal porphins.[21,22] The main difference between the two series is the effect of the presence of electron-attracting meso-substituents on the ligand. In the case of the cobalt complexes, they caused ready formation of the pink neutral cobalt(I) species, but in the nickel series the products were the blue neutral nickel(II) 5-oxo-tridehydrocorrins (II). Attempts to pre-pare the cobalt analogues of (II) have so far been unsuccessful.

## EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus. U.v. and visible spectra were determined with a Unicam SP 8000 instrument for solutions in chloroform unless otherwise stated. N.m.r. spectra were measured for solutions in deuteriochloroform with a Varian A60 instrument with tetramethylsilane as internal standard. Mass spectra were determined with an A.E.I. MS9 instrument (direct insertion). Light petroleum refers to the fraction, b.p. 60—80°.

The electrochemical experiments employed a three-electrode cell at 21°. The working electrode was either a platinum gauze electrode (63 cm²) for controlled potential electrolyses, a piece of platinum foil (0·61 cm²) for cyclic voltammetry, or a dropping mercury electrode ($m = 1·354$ mg Hg s⁻¹, $t = 5·16$ s on open circuit in methanol electrolyte) for polarography. The counter electrode was a piece of platinum foil separated from the sample compart-ment by a saturated potassium chloride–agar salt bridge and a fritted glass disc. The reference electrode was a saturated potassium chloride–calomel electrode (SCE) removed from the sample by a glass frit and a salt bridge which contained 0·4M-tetrabutylammonium iodide in methanol–water (1 : 1).

The working electrode potential was controlled relative to the SCE by a Chemical Electronics TR 70/2A Potentiostat.

[15] R. D. Gillard, J. Chem. Soc. (A), 1967, 917.
[16] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' Benjamin, New York, 1966.
[17] R. Bonnett, J. R. Cannon, A. W. Johnson, and A. R. Todd, J. Chem. Soc., 1957, 1148.
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[20] D. Bormann, A. Fischli, R. Keese, and A. Eschenmoser, Angew. Chem., Internat. Edn., 1967, 6, 868; A. Eschenmoser, Quart. Rev., 1970, 24, 366.
[21] J. B. Paine and D. Dolphin, J. Amer. Chem. Soc., 1971, 93, 4080.
[22] A. Sweeney, Ph.D. Thesis, University of Nottingham, 1970.

Potential sweeps were generated by a Chemical Electronics RBI Waveform Generator over the range 3 to 300 mV s$^{-1}$. The current–potential curves were displayed on a Bryans X–Y recorder (model 26000 A3).

The solvent used in the study of the *meso*-di-, mono-, and un-substituted cobalt complexes was methanol containing 0·1M-tetramethylammonium acetate. The *meso*-trisubstituted complexes were examined in a methanol-dichloromethane (2 : 3) solvent which was 0·08M in tetramethylammonium acetate. All solutions were approximately 1mM in cobalt complex and dissolved air was removed by purging the solutions with argon.

*Dinitritocobalt*(III) 2,8,12,18-*Tetraethyl*-1,3,7,13,17,19-*hexamethyltetradehydrocorrin*.—A solution of the corresponding cobalt(II) perchlorate [3] (100 mg) in methanol (6 ml) containing glacial acetic acid (15 µl) was treated with sodium nitrite (200 mg) and shaken in a separating funnel for 30 min to give a green-brown solution. The mixture was diluted with water and extracted with methylene chloride until colourless. Concentration of the extracts and treatment with light petroleum gave green *needles* (119 mg, 84%), m.p. >300° (Found: C, 61·6; H, 6·3; N, 14·4. C$_{33}$H$_{41}$CoN$_6$O$_4$ requires C, 61·4; H, 6·4; N, 14·7%), $\lambda_{max.}$ 280, 283, 626, and 676 nm ($\varepsilon$ 30,900, 26,400, 10,000, and 13,400), $\lambda_{infl.}$ 638 nm ($\varepsilon$ 7570).

*Diazidocobalt*(III) 2,8,12,18-*Tetraethyl*-1,3,7,13,17,19-*hexamethyltetradehydrocorrin*.—A similar experiment but with sodium azide (200 mg) gave the *product* (120 mg, 86%) as green prisms, m.p. >290° (Found: C, 62·4; H, 6·5; N, 21·7. C$_{33}$H$_{41}$CoN$_{10}$ requires C, 62·2; H, 6·5; N, 22·0%), $\lambda_{max.}$ 286, 364, and 688 nm ($\varepsilon$ 30,900, 26,400 and 10,000), $\lambda_{infl.}$ 638 nm ($\varepsilon$ 7570).

*Dicyanocobalt*(III) 2,8,12,18-*Tetraethyl*-1,3,7,13,17,19-*hexamethyltetradehydrocorrin*.—A solution of the corresponding cobalt(II) perchlorate [3] (2·1 g) in methanol (120 ml) and acetic acid (0·18 ml) was treated with potassium cyanide (600 mg) and shaken in a separating funnel for 15 min to give a green solution containing crystals. Water (1 l) was then added and the resulting yellow-brown solid was separated, washed with water, and crystallised from methylene chloride–light petroleum to give brown-yellow *needles* (1·5 g, 65%), m.p. >300° (Found: C, 69·1; H, 6·7; N, 13·8. C$_{35}$H$_{41}$CoN$_6$ requires C, 69·5; H, 6·8; N, 13·9%), $\lambda_{max.}$ 276, 301, 361, 405, 503, 538, 682, and 754 nm ($\varepsilon$ 19,600, 16,200, 8350, 10,120, 2600, 1158, 5780, and 15,500), $\lambda_{infl.}$ 620 nm ($\varepsilon$ 1442); $\nu_{max.}$ 2200 cm$^{-1}$ (CN), $\tau$ 3·1 (s, C-5 and C-15 H), 6·19 and 6·21 (both q, 2 × C$H_2$·CH$_3$), 7·63 and 7·73 (s, each 2 × peripheral CH$_3$), 8·69 and 8·71 (both t, 2 × CH$_2$·C$H_3$), and 9·41 (s, C-1 and C-19 CH$_3$).

*Cobalt*(I) 5-*Cyano*- *and* 5,15-*Dicyano*-2,8,12,18-*tetraethyl*-1,3,7,13,17,19-*hexamethylcorrin* (IV; R$^1$ = H, R$^2$ = CN; R$^1$ = R$^2$ = CN).—The foregoing yellow-brown dicyanocobalt(III) complex (600 mg) in degassed anhydrous chlorobenzene (250 ml; stored over potassium carbonate and then Woelm basic alumina, grade I, before distillation under N$_2$) and protected from light was heated on a boiling water bath overnight (*ca.* 12 h). The colour of the solution had then changed from green-yellow to pink. The solvent was removed *in vacuo* and the resulting solid dissolved in methylene chloride and shaken with aqueous perchloric acid (10 ml of 60% made up to 100 ml). The pink colour quickly changed to violet and the mixture was shaken for *ca.* 1 h, filtered and evaporated to dryness. T.l.c. (SiO$_2$; 20% acetone–chloroform) showed two compounds, a pink neutral compound which turned blue in

air, and a purple-red polar spot. The mixture was redissolved in methylene chloride and chromatographed on Woelm basic alumina (grade IV) with methylene chloride as eluant. The first main fraction was pink and neutral and was quickly crystallised from methylene chloride–methanol to give brown needles of *cobalt*(I) 5,15-*dicyano*-2,8,12,18-*tetraethyl*-1,3,7,13,17,19-*hexamethyltetradehydrocorrin* (34 mg, 6%), m.p. >280° (Found: C, 59·6; H, 5·7; N, 11·9%; *m/e*, 602. C$_{35}$H$_{39}$CoN$_6$ requires C, 59·8; H, 5·6; N, 12·0%; *M*, 602·65), $\lambda_{max.}$ 270, 341, 480, and 542 nm ($\varepsilon$ 20,200, 34,300, 4850, and 15,400), $\lambda_{infl.}$ 373 and 403 nm ($\varepsilon$ 16,750 and 12,700); $\nu_{max.}$ 2200 cm$^{-1}$ (CN). A solution of this neutral dicyano-complex (120 mg) in methylene chloride (50 ml) was shaken with perchloric acid (10 ml of 60% made up to 100 ml) for 3 h. The organic layer quickly turned deep violet in colour. Separation of the organic phase, evaporation to dryness and crystallisation from methanol gave blue-black needles of *cobalt*(II) 5,15-*dicyano*-2,8,12,18-*tetraethyl*-1,3,7,13,17,19-*hexamethyltetradehydrocorrin perchlorate* (108 mg, 79%), m.p. 194° (Found: C, 59·7; H, 5·8; N, 11·6%; *m/e*, 601. C$_{35}$H$_{39}$ClCoN$_6$O$_4$ requires C, 59·8; H, 5·6; N, 12·0%; *M* − HClO$_4$, 601·11), $\lambda_{max.}$ 285, 330, 520, and 613 nm ($\varepsilon$ 24,320, 20,420, 15,420, and 15,810), $\lambda_{max.}$ on shaking with NaBr 291, 337, 540, and 616 nm ($\varepsilon$ 25,000, 28,800, 20,600, and 8500); $\nu_{max.}$ 2200 cm$^{-1}$ (CN).

The second major band to be eluted (a red salt) was identical (t.l.c. and electronic spectrum) with cobalt 2,8,12,18-tetraethyl-1,3,7,13,19-hexamethyltetradehydrocorrin perchlorate. A third band comprising a purple salt was shaken with aqueous sodium perchlorate and crystallised from methylene chloride–ethyl acetate to give purple needles of *cobalt*(II) 5-*cyano*-2,8,12,18-*tetraethyl*-1,3,7,13,17,19-*hexamethyltetradehydrocorrin perchlorate* (244 mg, 43%), m.p. 193—194° (Found: C, 59·9; H, 5·9; N, 10·3%; *m/e*, 576. C$_{34}$H$_{40}$ClCoN$_5$O$_4$ requires C, 60·3; H, 5·9; N, 10·3%; *M* − HClO$_4$, 576·1), $\lambda_{max.}$ 285, 335, 505, and 585 nm ($\varepsilon$ 21,840, 15,800, 12,400, and 8200); $\nu_{max.}$ 2200 cm$^{-1}$ (CN).

A methanolic solution (20 ml containing 30 µl of acetic acid) of the foregoing monocyano-perchlorate (250 mg) was treated with potassium cyanide (100 mg) and shaken in a separating funnel for 15 min; a green solution was obtained. Water was then added (200 ml); the solution was saturated with sodium chloride and then extracted with methylene chloride. The organic phase was then brownish-pink. Chromatography of the methylene chloride solution on Woelm basic alumina and elution with methylene chloride gave a pink neutral band which was separated; the residue was quickly crystallised from methylene chloride–methanol to give brown needles (109 mg, 42%), identical with the cobalt(I) 5,15-dicyano-2,8,12,18-tetraethyl-1,3,7,13,17,19-hexamethyltetradehydrocorrin already isolated. Thermolysis of the pink-brown solid as before in chlorobenzene gave an identical yield of the neutral cobalt(I) 5,15-dicyano-complex.

*Cobalt*(I) 5,15-*Dicyano*-2,8,12,18-*tetraethyl*-1,3,7,13,17,19-*hexamethyl*-10-*nitrotetradehydrocorrin*.—A mixture of cobalt 5,15-dicyano-2,8,12,18-tetraethyl-1,3,7,13,17,19-hexamethyltetradehydrocorrin perchlorate (120 mg), acetic anhydride (4 ml), and copper(II) nitrate trihydrate (120 mg) was shaken for 45 min. The purple mixture was poured into methanol (250 ml) and left overnight. The solution was concentrated *in vacuo* keeping the temperature as low as possible, diluted with water, extracted with

methylene chloride, and evaporated to dryness. The resulting solid was chromatographed (preparative alumina t.l.c.; elution with 20% acetone–chloroform). The pink-purple neutral band was collected and further purified by t.l.c. (SiO₂; 30% ether–light petroleum). The main band was collected and crystallised from methylene chloride–methanol to give long black *needles* (62 mg, 56%), m.p. >300° (Found: C, 64·9; H, 6·2; N, 15·2%; *m/e* 647. $C_{35}H_{38}CoN_7O_2$ requires C, 64·9; H, 5·9; N, 15·1%; *M*, 647·65), $\lambda_{max.}$ 270, 340, 490, and 550 nm (ε 24,200, 31,200, 7650, and 18,500), $\lambda_{infl.}$ 379 nm (ε 20,600); $\nu_{max.}$ 2200 (CN) and 1525 cm⁻¹ (NO₂), τ 6·03 and 6·44 (both q, both 2 × $CH_2 \cdot CH_3$), 7·23 and 7·43 (both s, both 2 × peripheral CH₃), 7·98 and 8·39 (both t, both 2 × $CH_2 \cdot CH_3$), and 9·93 (s, C-1 and C-19 CH₃).

*Cobalt*(I) 5,15(5,10?)-*Dinitro-* and 5,10,15-*Trinitro-2,8,12,18-tetraethyl-1,3,7,13,17,19-hexamethyltetradehydrocorrin.*—A mixture of cobalt(II) 2,8,12,18-tetraethyl-1,3,7,13,17,19-hexamethyltetradehydrocorrin perchlorate (1 g), acetic anhydride (30 ml), and copper(II) nitrate trihydrate (500 mg) was shaken for 45 min. The colour of the mixture changed from red, to purple, to blue-green. The mixture was poured into methanol (1 l) and left overnight. The resulting purple solution was concentrated *in vacuo* keeping the temperature as low as possible and then diluted with aqueous sodium perchlorate (1 l). The precipitated solid was separated, washed with water, and chromatographed (preparative t.l.c.; eluant 20% acetone–chloroform × 3). The two main bands were separated.

(i) The pink neutral band was extracted and the product was further purified by t.l.c. (SiO₂; 30% ether–light petroleum). The main pink neutral band was again extracted and the product crystallised quickly from methylene chloride–methanol to give shining black plates of *cobalt*(I) 2,8,12,18-*tetraethyl-1,3,7,13,17,19-hexamethyl-5,10,15-trinitrotetradehydrocorrin* (164 mg, 13%), m.p. >300° (Found: C, 57·7; H, 5·6; N, 14·2%; *m/e*, 687. $C_{33}H_{38}CoN_7O_6$ requires C, 57·6; H, 5·6; N, 14·3%; *M*, 687·63), $\lambda_{max.}$ 270, 333, 490, and 539 nm (ε 24,150, 33,000, 8260, and 1950) $\lambda_{infl.}$ 370 nm (ε 18,800); $\nu_{max.}$ 1520 cm⁻¹ (NO₂), τ 6·33 and 6·42 (both q, both 2 × $CH_2 \cdot CH_3$), 7·72 and 7·76 (both s, both 2 × peripheral CH₃), 8·11 and 8·44 (both t, both 2 × $CH_2 \cdot CH_3$), and 9·14 (C-1 and C-19 CH₃).

(ii) The purple polar band was separated, extracted, and evaporated. The residue was dissolved in methylene chloride and shaken with aqueous sodium perchlorate. The organic phase was separated and evaporated, and the residue crystallised from methylene chloride–light petroleum as thick purple-black *prisms* (364 mg, 27%), m.p. >250° (Found: C, 53·8; H, 5·4; N, 11·2. $C_{33}H_{39}ClCo-N_6O_8$ requires C, 53·4; H, 5·3; N, 11·3%), $\lambda_{max.}$ 285, 345, 510, and 593 nm (ε 27,200, 17,300, 12,550, and 10,300); $\lambda_{max.}$ of the corresponding nitrate: 285, 318, 519, and 600 nm (ε, 26,500, 23,300, 16,400, and 7920).

A sample of the dinitro-perchlorate salt was chromatographed (t.l.c. on Al₂O₃; eluant 20% acetone–chloroform). The pink neutral band was quickly collected and crystallised from methylene chloride–methanol to give brown needles of the corresponding neutral *cobalt*(I) *derivative*, m.p. >300° (Found: C, 61·5; H, 6·1; N, 13·1%; *m/e*, 642. $C_{33}H_{39}CoN_6O_4$ requires C, 61·7; H, 6·1; N, 13·1%; *M*, 642·63), $\lambda_{max.}$ 270, 334, 490, and 535 nm (ε 19,900, 30,600, 9250, and 13,100), $\lambda_{infl.}$ 375 nm (ε 13,950). A sample of the neutral dinitrocobalt(I) complex was shaken overnight with aqueous perchloric acid (10 ml of 60% made up to 100 ml); the dinitro-cobalt(II) perchlorate was re-formed.

*Dibromocobalt*(III) 2,8,12,18-*Tetraethyl-1,3,7,13,17,19-hexamethyl-5,10,15-trinitrotetradehydrocorrin.*—A solution of cobalt(I) 2,8,12,18-tetraethyl-1,3,7,13,17,19-hexamethyl-5,10,15-trinitrotetradehydrocorrin (18 mg) in methylene chloride was treated with a solution of bromine in carbon tetrachloride. When exactly 1 mol. equiv. of bromine had been added the colour of the pink solution changed to green. Addition of light petroleum gave green *needles* (16 mg, 73%), m.p. >280° (Found: C, 46·8; H, 4·8; Br, 18·3; N, 11·1. $C_{33}H_{38}Br_2CoN_7O_6$ requires C, 46·5; H, 4·9; Br, 18·8; N, 11·5%), $\lambda_{max.}$ 296, 400, 526, 740, and 800 nm, τ 7·02 and 7·04 (both q, both 2 × $CH_2 \cdot CH_3$), 7·45 and 7·65 (both s, both peripheral CH₃), 8·47 and 8·69 (both t, both 2 × $CH_2 \cdot CH_3$), and 9·05 (s, C-1 and C-19 CH₃).