Stable Cobalt(I) Complexes of Tetradehydrocorrins

By C. M. Elson, A. Hamilton, A. W. Johnson,* and C. Stubbs

(*School of Molecular Sciences and A.R.C. Unit of Nitrogen Fixation, University of Sussex, Falmer, Brighton* BN1 9QJ)

Summary Cyanation and nitration of cobalt(II) tetradehydrocorrin salts yield cobalt(III) derivatives which can be converted readily into crystalline neutral cobalt(I) complexes; these substituted cobalt(I) tetradehydrocorrins are reversibly oxidised to stable cobalt(II) complexes at potentials anodic to the oxidation potential of the unsubstituted cobalt(I) complex.

In a study of the substitution reactions of the tetradehydrocorrin (**1**; $R^1 = R^2 = H$)† we have encountered a novel series of pink complexes, prepared as in the following example. Treatment of the purple salt (**1**; $R^1 = R^2 = H$) with cyanide gave, by analogy with earlier work,[1] the neutral dicyanocobalt(III) species (**2**; $R^1 = R^2 = H$), which, when heated in chlorobenzene at 100° under nitrogen, gave a mixture of two crystalline pink, neutral cobalt complexes which contained respectively one (37%) and two (6%) cyano-*meso*-substituents. The location of these cyano-substituents was established by conversion of the monocyano-derivative with more cyanide into the corresponding dicyanocobalt(III) derivative (**2**; $R^1 = CN$, $R^2 = H$), which on heating gave the pink dicyano-compound (**3**; $R^1 = R^2 = CN$) and this was shown to contain only one *meso*-hydrogen (n.m.r.). Treatment of the pink complexes with perchloric acid gave the cobalt(II) perchlorates (**1**; $R^1 = CN$, $R^2 = H$ and $R^1 = R^2 = CN$) respectively.

We have been unable to bring about cyanation at the remaining *meso*-unsubstituted position (C-10) by heating (**2**; $R^1 = R^2 = CN$) obtainable from (**1**; $R^1 = R^2 = CN$) by treatment with excess of cyanide. However, nitration [$Cu(NO_3)_2$–Ac_2O] of the perchlorates of the cobalt(II) ligands (**1**; $R^1 = R^2 = H$ or CN) gave the 5,15(5,10?)-dinitro-,

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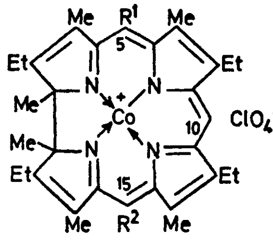
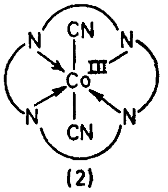
† Satisfactory analyses and spectra consistent with the assigned structures have been obtained for all new compounds described.

5,10,15-trinitro-, and 5,15-dicyano-10-nitro-cobalt(III) derivatives respectively (having axial nitrito-ligands; **2**), which were reduced by methanol to the cobalt(II) salts. These salts (**1**) were converted during chromatography on alumina into crystalline pink derivatives showing the same spectral properties as the cyano-substitution products described above.

In contrast to the paramagnetic cobalt(II) salts (**1**), the four stable pink compounds were diamagnetic and gave sharp n.m.r. spectra. As they clearly differed from the green octahedral cobalt(III) complexes, into which they could be transformed, it was concluded that they were either cobalt(I) (**3**) or dimeric cobalt(II) species‡ and as the stability of the pink products increased markedly with the number of electronegative substituents the cobalt(I) formulation seemed preferable. Molecular-weight determinations (vapour-phase osmometry) showed that the pink 5,15-dicyano-10-nitro-derivative existed as the monomer in dilute solution although in more concentrated solution evidence was obtained for association to a dimer.[2]

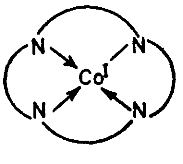


(1)



(2)

[Ligand as (1)]



(3)

[Ligand as (1)]

The electrochemical behaviour of the various cobalt complexes was examined by controlled potential electrolysis and cyclic voltammetry on platinum electrodes under argon (see Table). Cyclic voltammograms of samples of the isolated mono-, di-, and un-substituted cobalt(II) salts (**1**) met the criteria for a diffusion controlled reversible one-electron reduction process.[3-5] The unsubstituted salt (**1**; $R^1 = R^2 = H$) 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 using the methanol electrolyte. Attempts to prepare unsubstituted- and 5-monocyano-cobalt(I) complexes by controlled potential reduction of the cobalt(II) complexes were unsuccessful. The electrolyses proceeded to steady states presumably owing to oxidation of the reduced cobalt by traces of oxygen. However, controlled potential reductions of the cobalt(II) 5,15-dicyano- and dinitro-tetradehydrocorrin salts produced stable cobalt(I) species. The cobalt(I) dicyanotetradehydrocorrin produced by electrolysis had the same half-wave potential and visible absorption spectrum as the isolated cobalt(I) dicyano-complex. Further, the $E_{\frac{1}{2}}$ values determined from cyclic voltammograms of these cobalt(I) complexes were within 10 mV of the values for the reductions of the corresponding cobalt(II) complexes.

Half-wave potentials of cobalt tetradehydrocorrin complexes

Substitution of tetradehydrocorrin ring	Redox couple	Supporting electrolyte[a]	$E_{\frac{1}{2}}$[b]/V[c]
Unsubstituted	$Co^{II} + e \rightleftharpoons Co^{I}$	A	−0·27
5-Cyano	$Co^{II} + e \rightleftharpoons Co^{I}$	A	−0·10
5,15-Dicyano	$Co^{II} + e \rightleftharpoons Co^{I}$	A	+0·09
5,15-(5,10?)-Dinitro	$Co^{II} + e \rightleftharpoons Co^{I}$	A	+0·07
5,15-Dicyano-10-nitro	$Co^{I} - e \rightleftharpoons Co^{II}$	B	+0·31
5,10,15-Trinitro	$Co^{I} - e \rightleftharpoons Co^{II}$	B	+0·29

[a] A, 0·1M-tetramethylammonium acetate in methanol; B, 0·08M-tetramethylammonium acetate in CH_2Cl_2–MeOH (3:2). [b] Half-wave potential measured at 85·2% of peak current.[3] [c] Potentials are in V relative to a saturated aqueous calomel electrode at 21°.

Cyclic voltammograms of the cobalt(I) trinitro- and dicyanomononitro-tetradehydrocorrins indicated that the electron-transfer process was not completely reversible. However, controlled potential oxidation of the latter cobalt(I) complex produced a stable cobalt(II) species which displayed the same cyclic voltammetric behaviour as the original cobalt(I) complex. On the other hand, the oxidation of the cobalt(I) trinitro-tetradehydrocorrin did not yield a stable cobalt(II) species.

The variation of the half-wave potentials of the various cobalt(I) complexes (**3**) clearly showed that they are stabilised with respect to oxidation by the presence of strong electron-withdrawing groups on the ligand. The observed reversibility of the charge-transfer processes excludes the possibility of chemical reactions occurring subsequent to the electrochemical step and establishes that the cobalt(I) species are simple monomeric complexes.

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‡ Such a formulation is excluded by the results of voltammetric studies (see later).

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