Metal Complexes of 1,19-Dimethylcorrin

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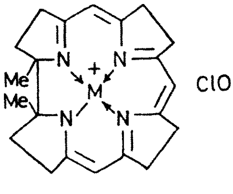
Summary Crystalline nickel(II) and cobalt(II) complexes of 1,19-dimethylcorrin have been isolated as the perchlorates, as well as a dicyanocobalt(III) complex, from room temperature hydrogenations of the corresponding metal tetradehydrocorrin perchlorates.

WE have applied our pyrrole-based corrin synthesis[1] to the preparation of nickel and cobalt complexes of 1,19-dimethylcorrin (I; M = Ni, Co), the first β-free corrins to be described. The starting product for the syntheses was 2,2′-dipyrromethane,[2] which was condensed with 2-formyl-5-methylpyrrole in presence of hydrogen bromide to yield 1,19-dimethyl-1,19-dideoxybiladiene-*ac* dihydrobromide (II) Alternatively the same salt was obtained by condensation of 5,5′-diformyl-2,2′-dipyrromethane[2] with 2-methylpyrrole. The dihydrobromide (II) was not normally isolated but was cyclised immediately either in *NN*-dimethylformamide solution in presence of nickel acetate to yield nickel(II) 1,19-dimethyltetradehydrocorrin, isolated as the perchlorate (III; M = Ni; 26·2%), or in dimethyl sulphoxide solution in presence of cobalt(II) acetate to give the cobalt analogue (III; M = Co; 25·9%). Satisfactory analytical figures have been obtained for all the compounds described herein.

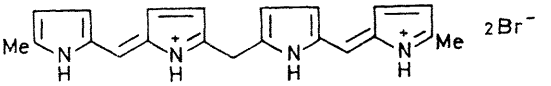
The most noticeable effect of the absence of β-alkyl substituents in nickel 1,19-dimethyltetradehydrocorrin perchlorate (*cf.* ref. 3) was the reduction of the solubility in organic solvents. Although the nickel complex (III; M = Ni) was relatively stable to acids, it was slowly converted into a blue neutral product with base. In contrast the cobalt complex (III; M = Co) was cleaved rapidly at room temperature in presence of 0·05N-hydrochloric acid and was decomposed by 2N-sodium hydroxide. The hydrogenation of either of the metal 1,19-dimethyltetradehydrocorrin perchlorates to the corresponding metal 1,19-dimethylcorrins, also isolated as perchlorates (I), was effected in presence of W2 Raney nickel (room temp.; 25 atmos. H_2). These conditions are markedly milder than those required for the hydrogenation of the nickel or cobalt 1,3,7,8,12,13,17,19-octa-alkyltetradehydrocorrin salts, where a temperature of 165° at 100 atmospheres pressure was required to obtain the corresponding corrins.[1] The dark-brown cobalt(II) dimethylcorrin salt was also converted into the bright red neutral dicyanocobalt(III) corrin (IV); all three metal 1,19-dimethylcorrins were crystalline in contrast to the corrins we prepared earlier,[1] which contained asymmetric centres at each of the eight β-positions. The electronic spectrum of the nickel 1,19-dimethylcorrin perchlorate (I; M = Ni) (λ_{max} 244, 266, 277, 304, 317, and 428 nm.; ϵ, 16,460, 9,150, 10,610, 23,420, 24,880, and

13,540 respectively; $\lambda_{\text{infl.}}$ 390 and 450 nm, ϵ, 7410 and 10,340) did not differ appreciably from those of the synthetic nickel corrin salts already described,[1,4] and similarly the spectrum of the dicyanocobalt(III) 1,19-dimethylcorrin (IV) (λ_{max} 269, 291, 299, 313, 356, 384, 406, 490, 524, and 563 nm; ϵ, 7950, 4760, 5870, 5600, 19,070, 2540, 2820, 3790, 6100, and 6890, respectively; $\lambda_{\text{infl.}}$ 260, 264, 340, and 551 nm; ϵ, 6010, 6,520, 10,520 and 5500) agrees with that quoted for (±)-[dicyanocobalt(III)]1,2,2,7,7,12,12-heptamethylcorrin.[5] The n.m.r. spectrum of the nickel 1,19-dimethylcorrin perchlorate showed signals at τ 3·68 (C-10 *meso*-H), 4·0 (C-5 and C-15 *meso*-H) and 8·53 (C-1 and C-19 Me), which agree with the signals of the corresponding protons in our earlier preparations,[1] except for the C-10 *meso*-proton which was at appreciably lower field than the signal (τ 3·93) of the corresponding proton of the nickel corrin perchlorates containing six β-alkyl substituents. The relative involatility of the metal derivatives of 1,19-dimethylcorrin necessitated the use of more extreme experimental conditions for the mass spectral determinations, and the mass spectra of the nickel(II) and cobalt(II) 1,19-dimethylcorrin perchlorates showed base peaks (*m/e* 387 for the nickel corrin salt and *m/e* 388 for the cobalt corrin salt) which did not correspond to the molecular ions but rather to ($M - 4 - \text{ClO}_4$) and the dicyanocobalt(III) corrin (IV) showed the base peak at *m/e* 388 ($M - 4 - 2\text{CN}$).

As well as the corrins, crystalline byproducts were obtained from the hydrogenations of both nickel and cobalt tetradehydrocorrins (III). In the nickel series the by product was isolated (5%) as the perchlorate and the mass spectrum showed an identical base peak (*m/e* 387) and a similar splitting pattern to that of the nickel 1,19-dimethylcorrin perchlorate, suggesting that the two salts were isomeric. The electronic spectrum, however (λ_{max} 259, 293, 340, and 400 nm; ϵ_{max} 6970, 9290, 2860 and 14,830; $\lambda_{\text{infl.}}$ 283, and 382 nm, ϵ, 7150 and 8840) was markedly shifted to lower wavelengths and intensities, indicating that the conjugated system of the corrin chromophore was broken. Further work on the structure of this product is in progress. The byproduct in the cobalt series was obtained only in low yield (*ca.* 1%) and it was isolated as the dicyanocobalt(III) derivative. It was markedly more volatile than the corrin and gave base peaks at *m/e* 392 and 390, the former corresponding to the molecular ion (less the cyanide groups) of an isomer of dicyanocobalt(III) 1,19-dimethylcorrin.



(I)



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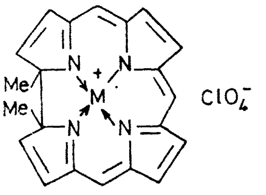
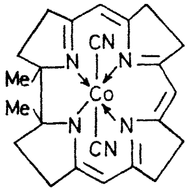


(III)



(IV)

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