184. Structure and Reactivity of Xanthocorrinoids

Part III[1])

The First Example of a Pinacol-Type Rearrangement in the Corrin Series

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Dedicated to Prof. *Albert Eschenmoser* on the occasion of his 60th birthday

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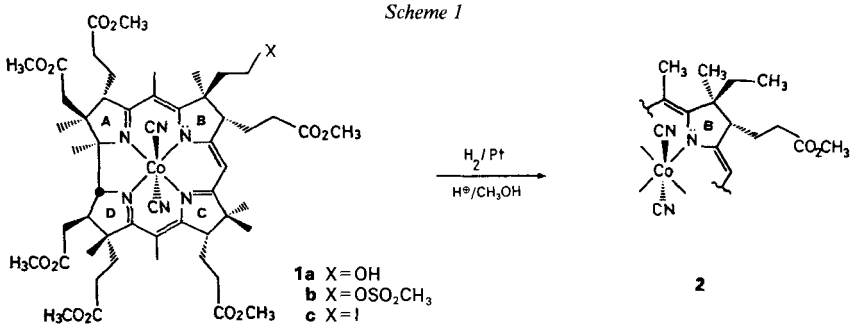
The transformation of the *c*-acetic-acid chain of hexamethyl *Coα, Coβ*-dicyanocobyrinate into an ethyl group (→**2**) as well as the synthesis of the pentadecaalkyl-cobalticorrin **6d** from commercial cyanocobalamin are described. On reaction of **2** or **6d** with O_2 in the presence of ascorbic acid, migration of the CH_3 group at C(5) to the vicinal position C(6) takes place concomitantly with the introduction of a carbonyl group at C(5).

Within the scope of our investigations concerning the influence of the acetic-acid substituent at the corrin ring position C(7) in the course of the *Udenfriend* reaction with derivatives of cobyrinic acid, it was obvious to include a substrate in which the C(7) substituent situated above the plane of the corrin chromophore is an alkyl group. The synthesis of such a derivative **2** *(Scheme 1)*[4]) with an ethyl group instead of the *c*-acetic-

Scheme 1



[1]) Part II: preceding paper [1].

[2]) Part of the Ph. D. Thesis of *B. G.*, Technische Universität Braunschweig, 1979.

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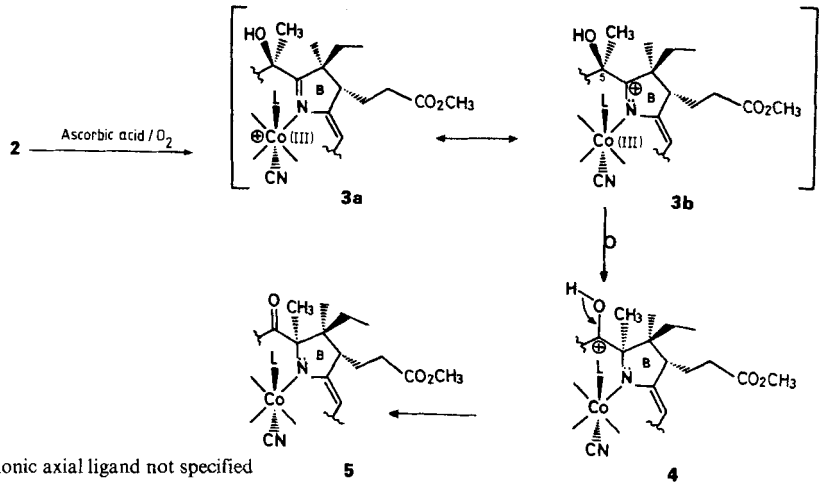
[4]) For the sake of clarity, only the part of the molecule which is modified during the reaction is represented in the partial structure; remainder as in **1**.

Scheme 2



L = Anionic axial ligand not specified

acid chain was carried out in about 90% yield by catalytic hydrogenolysis of the 2-iodoethyl derivative **1c** which was prepared from hexamethyl dicyanocobyrinate [2] via the primary alcohol **1a** and the corresponding mesylate **1b** *(cf. Exper. Part)*. When oxidized with O_2 in the presence of ascorbic acid, **2** yielded a brownish yellow corrinoid whose unexpected structure **5** was elucidated by spectroscopic methods *(Scheme 2)*.

The UV/VIS spectrum of **5** shows a distinct similarity to those of the other yellow corrinoids characterized so far. The hypsochromic shift of the maximum at 476 nm indicates, however, that the chromophore must be slightly different. The presence of a carbonyl group at C(5) is revealed both by an IR-absorption band at 1700 cm^{-1} and by a low-field peak (194.21 ppm) in the ^{13}C-NMR spectrum.

Particularly, the configuration at C(6) of **5** could be established, after the signals of all CH_3 groups in the molecule had been assigned by ^1H-NMR NOE difference spectroscopy and selective $^{13}C,^1H$ decoupling experiments *(cf. Exper. Part)*, on the ground of the NOE observed between the two CH_3 groups at C(6) and C(7), which must be, therefore, *cis* to each other (see *Table*).

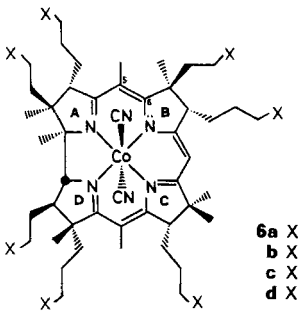
The formation of **5** as the main product of the reaction of **2** with *Udenfriend's* reagent, surprising at the first glance, can be explained in a straightforward manner by the

Table. *Assignments of ^1H-NMR Resonance Signals in* **5** *by $^1H,^1H$-NOE-Difference Experiments*[a])

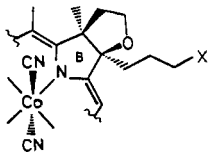
Irradiated Resonance [ppm]		Enhanced Signals [ppm]
2.15	CH_3–C(15)	2.85 (H–C(13)); 1.22 (CH_3–C(17))
1.66	CH_3–C(1)	1.33 (CH_3–C(2)); 2.90 (H–C(18))
1.33	CH_3–C(2)	1.66 (CH_3–C(1))
1.31	CH_3–C(7)	1.55 (CH_3–C(6)); 2.05, 1.67 ($CH_2(8^1)$); 1.65, 1.36 ($CH_2(7^1)$)
1.29	α–CH_3–C(12)	1.14 (β–CH_3–C(12)); 5.13 (H–C(10))
1.22	CH_3–C(17)	3.90 (H–C(19)); 2.15 (CH_3–C(15))
1.14	β–CH_3–C(12)	2.85 (H–C(13)); 5.13 (H–C(10))
0.83	CH_3–C(7^1)	2.63 (H–C(8)); 1.65, 1.36 ($CH_2(7^1)$)

[a]) In $CDCl_3$ solution at 400.13 MHz.

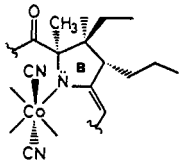
mechanism suggested previously for the reaction of heptamethyl cobyrinate under the same conditions [1]. In fact, resonance structure **3b** of the cationic intermediate which is presumably formed by reaction of **2** with ascorbic acid in the presence of O_2[5]), should be predestined for a rearrangement of the pinacol-pinacolone type. Stereoselective migration of the CH_3 group at C(5) leads, after loss of a proton from **4**, to the oxo-derivative **5**. As mentioned earlier [1], the alternative stabilization of **3** by reaction with H_2O to yield a diol must be a reversible process, which only leads to the final product of the reaction when other pathways are thermodynamically less favorable. Moreover, it has been demonstrated previously [1], that the β-substituent at C(7) has a decisive influence on the stabilization of the cationic intermediate **3**. Consequently, one may expect that all corrinoids bearing an alkyl group at C(7) above the plane of the macrocycle undergo a pinacol-pinacolone rearrangement when reacted with O_2 in the presence of ascorbic acid and, therefore, the reactivity of a corrin derivative with only alkyl substituents was considered worth investigating. The synthesis of such a derivative, namely **6d**, was briefly reported some years ago [3]. Initially, the direct reduction of the tosylhydrazides of carboxylic acids [4] [5] was envisaged as a possible route to **6d**. However, as the preparation of the heptatosylhydrazide of cobyrinic acid failed, a three-step synthesis was carried out. Thus, heptamethyl *Coα,Coβ*-dicyanocobyrinate was reduced with $LiAlH_4$ to yield, after reaction with CN^- ions, a mixture of heptol **6a** and hexol ether **7a**[6]), which could not be separated by conventional methods. However, the pure heptol is obtained when heptamethyl aquocyanocobyrinate [6] is used instead of the dicyano complex, provided that the product is isolated immediately after completion of the reaction. As **6a** is soluble in H_2O and only slightly soluble in organic solvents, it was transformed into the corresponding heptaacetate **6b** for the purpose of characterization. From the fact that **6a** is



6a X = OH
b X = $OCOCH_3$
c X = OSO_2CH_3
d X = H



7a X = OH
b $OCOCH_3$
c X = OSO_2CH_3
d X = H



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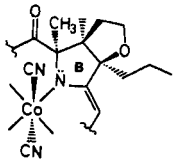
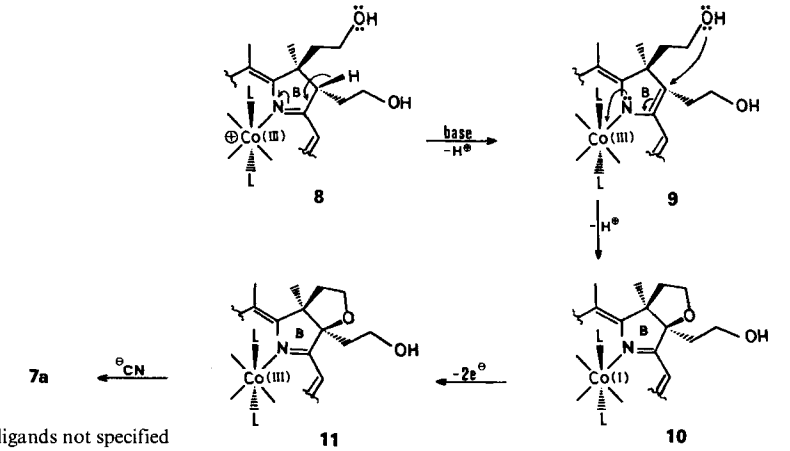


13

[5]) For a discussion of the reaction mechanism, *cf.* [1].

[6]) For the sake of clarity only the part of the molecule which is modified during the reaction is represented in the partial structure; remainder as in **6**.

Scheme 3: *Possible Mechanism of the Formation of* **7a** *from* **6a** *by Intramolecular Reduction of the Co-Ion.*



almost quantitatively transformed into the cyclic ether **7a** on standing of the reaction mixture overnight, after addition of H_2O, as well as on treatment of the isolated reaction product with aq. KOH for 3 h, it follows that the formation of **6a** and **7a** are two independent reactions. Most likely, the formation of **7a** is initiated by deprotonation at C(8) (see **8**) as suggested for the closure of the *c*-lactone ring of 'dehydrovitamin B_{12}' [7] *(cf. Scheme 3)*[7]). Accordingly, heptamethyl aquocyanocobyrinate, which is more easily reduced to the Co(I) state by $LiAlH_4$ than the dicyano complex (*cf.* [6]), is transformed into **6a** without side reactions, probably because cyclisation of the deprotonated intermediate **9**, which involves the shift of one electron pair to the Co-ion, cannot occur in the Co(I) complex.

The most characteristic spectroscopic differences between **6a** and **7a** can be summarized as follows: Whereas the cyclic ether **7a** and its hexaacetate **7b** show two distinct UV-absorption maxima at 304.5 and 314.5 nm, the corresponding absorption of both **6a** and **6b** gives rise to a broad band at 310 nm. In the ^{1}H-NMR spectrum, H–C(10) vicinal to the cyclic ether is shifted downfield by 0.18 ppm relative to the corresponding signals in both the heptol **6a** and its heptaacetate **6b**. Moreover, CH_3–C(5) and CH_3–C(15) which give rise to 2 *s* in the case of **6a** and **6b** become isochronous in the corresponding cyclic ethers **7a** and **7b**. In the ^{13}C-NMR spectra of the acetates **6b** and **7b** the substitution of the C–H bond at C(8) by a C–O bond is revealed by a paramagnetic shift of the C(8) signal from 55.8 ppm (*d*) to 95.3 ppm (*s*) and by a shift of the C(7) signal from 48.5 to 53.1 ppm.

The usual procedure for transforming an alcohol into the corresponding alkane consists in the reduction of the tosylate or mesylate of the former by some hydride donor. In the case of the corrinoids **6a** and **7a**, the best results were obtained when the corresponding hepta- and hexamesylate, respectively, were prepared according to the method given in [8] and subsequently reduced with $Li(Et_3BH)$ as described by *Holder* and *Matturro* [9] for simpler molecules. In our hands, the reduction of the mesylates **6c** and **7c** with $LiAlH_4$ (*cf.* [10]) was unsuccessful. On reduction of **6c** and **7c** with $Li(Et_3BH)$, the corresponding alkyl-corrinoids were obtained as ethyl-Co(I) derivatives which, on account of their instability towards light, were conveniently transformed, without previous

[7]) Obviously, step **9** to **10** can be also formulated as a one-electron process. In this case, the Co(III) ion would change to the Co(II) oxidation state.

isolation, into the dicyano-Co(III) complexes **6d** and **7d**, respectively, by irradiation in the presence of CN^- ions. As known from other alkyl-cobalt corrinoids [11], the methyl protons of the Et group on the Co(I) ion in both intermediates show the lowest chemical shift in the NMR spectrum (at −1.12 ppm).

Both alkyl-corrinoids **6d** and **7d** were obtained as crystalline compounds which, in contrast to all other derivatives of cobyrinic acid known so far, are soluble in hexane and

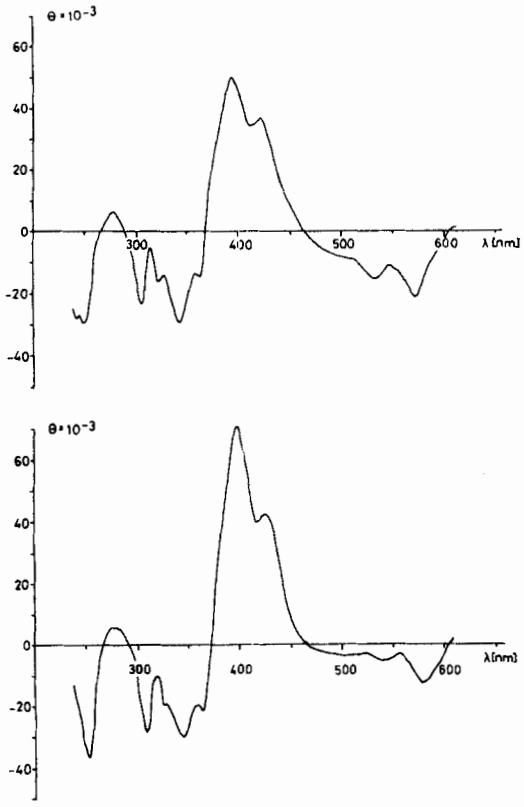


Fig. 1. CD spectra of Coα,Coβ*-dicyano-2,7,18-triethyl-1,2,5,7,12,12,15,17-octamethyl-3,8,13,17-tetrapropylcobalticorrin* (**6d**, above) *and heptamethyl* Coα,Coβ*-dicyanocobyrinate* (below)

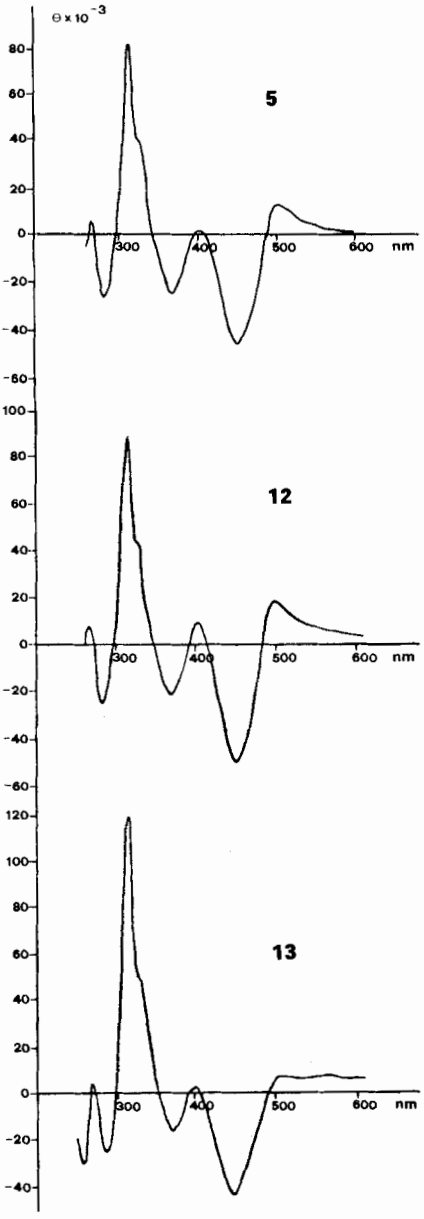


Fig. 2. *CD spectra of hexamethyl (6*R*)-*Coα,Coβ*-dicyano-7*^{1}*-decarboxy-5-demethyl-5,6-dihydro-6,7*^{1}*-dimethyl-5-oxocobyrinate* (**5**), Coα,Coβ*-dicyano-2,7,18-triethyl-5,6-dihydro-1,2,6,7,12,12,15,17-octamethyl-5-oxo-3,8,13,17-tetrapropylcobalticorrin* (**12**), *and* Coα,Coβ*-dicyano-2,18-diethyl-5,6,7*^{1}*,7*^{2}*-tetrahydro-1,2,6,7,12,12,15,17-octamethyl-5-oxo-3,8,13,17-tetrapropylfuro[3,2-*g*]cobalticorrin* (**13**)

other nonpolar solvents. Accordingly, conventional EI-MS could be obtained of both compounds, which display a relative intense parent peak and a base peak corresponding to the loss of the two CN ligands. All other available spectroscopic data (UV/VIS, IR ^{1}H-NMR, and ^{13}C-NMR spectra) corroborate the structures given for **6d** and **7d** (see *Exper. Part*). Moreover, the comparison of the chiroptical data of **6d** with those of heptamethyl *Coα,Coβ*-dicyanocobyrinate points out that no epimerization takes place during the reaction sequence at any of the nine chiral centers of the chromophore *(cf. Fig. 1)*.

To carry out the *Udenfriend* reaction with the corrinoids **6d** and **7d**, more vigorous conditions were necessary than in the case of the cobyrinic-acid derivatives. Thus, maximum conversion (35% yield) was obtained after about 5 h at 70–80°C using MeOH/aq. phosphate buffer with a higher percentage of MeOH (up to 5:1) than under standardized conditions [1] *(cf. Exper. Part)*. On reaction with O_2 in the presence of ascorbic acid, **6d** and **7d** yielded brownish yellow products whose structures **12** and **13**, respectively, are supported by all available analytical data. The absolute configuration at C(6) in both products **12** and **13** is assumed to be the same as in **5** on the basis of the similar CD spectra (see *Fig. 2*). Like **5**, both oxo-corrinoids **12** and **13** show a IR-absorption band at 1690 and 1710 cm^{-1}, respectively, which is associated with the carbonyl group introduced in the molecule as a result of the pinacol-pinacolon rearrangement. Particularly in the case of **13**, the two diastereotopic protons adjacent to the O-atom of the ether ring, which give rise to 2 *m* at 3.85 and 3.46 ppm in the starting material **7d**, collapse to a *t* (at 3.86 ppm) in the product, thus indicating that the reaction has taken place at the double bond between C(5) and C(6), as anticipated by the mechanism suggested earlier [1].

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Experimental Part

General. See [1]. EI-MS were obtained at an ionizing voltage of 70 eV on a *AEI MS 9* instrument. Fast atom bombardement mass spectra (FAB-MS) were measured on a *Vacuum Generators Micromass 7070 E* spectrometer (*cf.* [1]).

Hexamethyl Coα,Coβ-Dicyano-7^1-decarboxy-7^1-(hydroxymethyl)-cobyrinate (**1a**). Hexamethyl *Coα,Coβ*-dicyanocobyrinate [2] (400 mg) was dissolved under Ar in 40 ml of dry benzene/dioxane 3:1. The soln. was cooled to – 5°, and 2.30 ml of a soln. of Et_3N in benzene (0.361M) was added. After dropwise addition of 1.87 ml of ethyl chloroformate in benzene (0.525M), the mixture was stirred for 15 min at – 5°, then warmed to r.t., and finally poured rapidly into 60 ml of abs. MeOH/dioxane 1:1 containing 670 mg of $NaBH_4$. After 10 min, the mixture was successively diluted with 50 ml of CH_2Cl_2, neutralized with 1N HCl, and washed with dist. H_2O and 2% aq. KCN soln. The org. layer was separated and dried by filtration through dry cotton. The soln. was evaporated and the residue purified by prep. TLC using CH_2Cl_2/MeOH 97:3, which contained 0.1% of KCN. Recrystallization from CH_2Cl_2/hexane yielded 0.34 g (86%) of **1a**, m.p. 138–140°. IR ($CHCl_3$): 3400*m*, 3010*m*, 2980*m*, 2950*m*, 2920*m*, 2840*m*, 2110*w*, 1730*s*, 1580*m*, 1500*m*, 1470*m*, 1435*s*, 1400*m*, 1365*m*. UV/VIS: 585 (4.03), 546 (3.97), 512 (sh), 419 (3.36), 369 (4.53), 353 (sh), 313 (3.98), 308 (3.97), 277 (4.06), 217 (3.71). ^{1}H-NMR (100 MHz): 5.52 (*s*, H–C(10)); 3.76, 3.72, 3.69 (6H), 3.67, 3.62 (5 *s*, 6 CH_3O); 2.22 (*s*, CH_3–C(15)); 2.19 (*s*, CH_3–C(5)); 1.51 (6H), 1.36 (6H), 1.26, 1.19 (4 *s*, 6 CH_3); HO–C(7^2) is hidden. ^{13}C-NMR (25.16 MHz): 176.0 (*s*, C(11)); 175.6, 175,2 (2 *s*, C(4), C(16)); 173.9, 173.7, 173.0, 172.8 (2C), 171.9, 171.8 (6 *s*, 6 $COOCH_3$, C(9)); 164.2, 163.5 (2 *s*, C(6), C(14)); 130.9, 128.7 (2 *s*, 2 C≡N); 104.2 (*s*, C(5)); 101.7 (*s*, C(15)); 90.4 (*d*, C(10)); 82.5 (*s*, C(1)); 74.8 (*d*, C(19)); 58.5 (*t*, C(7^2)); 58,2 (*s*, C(17)); 56.6, 56.5 (2 *d*, C(3), C(8)); 53.6 (*d*, C(13)); 52.3, 51.8 (3C), 51.6 (2C) (3 *q*, 6 CH_3O); 49.0 (*s*, C(7)); 46.8, 45.6 (2 *s*, C(2), C(12)); 43.6 (*t*, C(7^1)); 41.2 (*t*, C(2^1)); 39.2 (*d*, C(18)); 33.8, 32.5, 31.7, 31.1, 30.6, 29.7, 26.6,

25.6, 24.9 (9 *t*, 9 CH_2); 31.1 (*q*, *β*–CH_3–C(12)); 22.0, 21.2, 19.7, 18.4, 16.9 (5 *q*, 5 CH_3); 15.7 (*q*, CH_3–C(5)); 15.1 (*q*, CH_3–C(15)). FAB-MS (glycerol): 1036 (26, $(M + 2)^+ - CN$), 1010 (100, $(M + 2)^+ - 2CN$), 996 (13), 980 (8), 964 (7), 951 (13), 936 (12), 923 (6), 908 (10), 893 (8), 878 (14).

Hexamethyl Coα,Coβ-*Dicyano-7*^{1}*-decarboxy-7*^{1}*-(methanesulfonyloxymethyl)cobyrinate* (**1b**). A stirred soln. of **1a** (260 mg) in 10 ml of dry THF containing 0.2 ml of Et_3N was cooled under Ar to – 5° and then treated with 2 ml of MsCl in THF (0.419M). The mixture was warmed up to r.t., and stirring was continued for 15 h. Then, the excess of MsCl was removed by adding 2 ml of MeOH, and the solvent was evaporated. The residue was dissolved in 50 ml of CH_2Cl_2 and the soln. poured into dist. H_2O. After extraction, the org. layer was washed once with 2% aq. KCN and again with dist. H_2O. The soln. was dried by filtration through cotton, and the solvent was evaporated. Purification of the crude product by prep. TLC using CH_2Cl_2/MeOH 96:4 containing 0.1% of KCN yielded 374 mg (98%) of **1b**. IR (CCl_4): 2980*m*, 2920*m*, 2120*w*, 1730*s*, 1580*m*, 1500*m*, 1440*m*, 1350*m*, 1170*m*. UV/VIS: 582 (3.95), 542 (3.87), 505 (3.68), 418 (3.35), 368 (4.41), 352 (sh, 4.08), 314 (3.91), 305 (3.90), 277 (3.96). CD ($5.11 \cdot 10^{-5}$M): 578 (–6459), 552 (–1292), 352.5 (–3553), 517 (–2261), 451 (0), 426 (27130), 417 (25838), 395 (47155), 373 (0), 366 (–19379), 361 (–16795), 347,5 (–29068), 327 (–17118), 320 (–10981), 309 (–27776), 386 (–4392), 274 (–8397), 253 (–3504), 246 (–27324), 233 (0). ^{1}H-NMR (400.13 MHz): 5.55 (*s*, H–C(10)); 3.77, 3.73, 3.70 (6H), 3.69, 3.63 (5 *s*, 6 CH_3O); 2.94 (*s*, CH_3SO_3); 2.24 (*s*, CH_3–C(15)); 2.21 (*s*, CH_3–C(5)); 1.57, 1.51, 1.38, 1.36, 1.25, 1.21 (6 *s*, 6 CH_3). ^{13}C-NMR: 176.58, 175.87, 175.42 (3 *s*, C(4), C(11), C(16)); 173.79, 173.48, 172.88, 172.67, 171.88, 171.70, 171.53 (7 *s*, 6 $COOCH_3$, C(9)); 163.52, 162.40 (2 *s*, C(6), C(14)); 132.2, 129.5 (2 *s*, 2 C≡N); 104.43 (*s*, C(5)); 102.41 (*s*, C(15)); 90.58 (*d*, C(10)); 82.69 (*s*, C(1)); 74.88 (*d*, C(19)); 67.58 (*t*, C(7^2)); 58.35 (*s*, C(17)); 56.70, 55.92 (2 *d*, C(3), C(8)); 53.69 (*d*, C(13)); 52.37, 51.82 (3C), 51.68, 51.57 (4 *q*, 6CH_3O); 48.89 (*s*, C(7)); 47.12, 45.93 (2 *s*, C(2), C(12)); 41.39 (*t*, C(2^1)); 40.87 (*t*, C(7^1)); 39.33 (*d*, C(18)); 37.38 (*q*, CH_3SO_3); 33.80, 32.54, 31.73, 30.95, 30.77, 29.73, 26.78, 25.75, 25.05 (9 *t*, 9 CH_2); 31.17 (*q*, *β*–CH_3–C(12)); 22.06, 21.59, 19.72, 18.19, 16.98 (5 *q*, 5 CH_3); 15.66 (*q*, CH_3–C(5)); 15.27 (*q*, CH_3C(15)). FAB-MS (glycerol): 1112 (10, $(M + 1)^+ - HCN$), 1085 (100, $(M + 1)^+ - 2HCN$), 1056 (8), 1007 (22), 992 (12, $(M + 1)^+ - 2CN - CH_3SO_3$), 962 (9), 949 (8), 922 (7), 904 (6), 878 (8).

Hexamethyl Coα,Coβ-*Dicyano-7*^{1}*-decarboxy-7*^{1}*-iodomethylcobyrinate* (**1c**). To a soln. of **1b** (300 mg) in 20 ml of dry monoglyme, NaI (118 mg) was added and the mixture refluxed under Ar for 4 h. After cooling to r.t., the solvent was evaporated. The residue was dissolved in CH_2Cl_2 and washed successively with dist. H_2O, 2% aq. KCN soln. and dist. H_2O. After evaporation of the solvent, the residue was purified by prep. TLC using CH_2Cl_2/MeOH 96:4, containing 0.1% of KCN, to yield 248 mg (92%) of **1c**. IR ($CHCl_3$): 2965*m*, 2920*m*, 2120*w*, 1730*s*, 1580*m*, 1500*m*, 1440*m*, 1350*m*, 1170*m*. UV/VIS: 582 (3.98), 543 (3.89), 507 (3.69), 418 (3.42), 367 (4.44), 349 (sh, 4.10), 309 (3.95), 277 (4.01). CD ($5.12 \cdot 10^{-5}$M): 577 (–3223), 552 (645), 531 (0), 515.5 (997), 456.5 (0), 423.5 (28685), 417 (27718), 394.5 (51246), 371 (0), 346 (–31908), 330 (–19016), 326 (–19983), 321 (–17404), 309.5 (–38032), 290 (–13214), 279 (–30619), 265.5 (–17082), 254 (–46411), 246 (–35776). ^{1}H-NMR (400.13 MHz): 5.46 (*s*, H–C(10)); 3.76, 3.72, 3.71, 3.70 (6H), 3.63 (5 *s*, 6 CH_3O); 2.23 (*s*, CH_3–C(15)); 2.17 (*s*, CH_3–C(5)); 1.50, 1.47, 1.37, 1.34, 1.25, 1.21 (6 *s*, 6 CH_3). ^{13}C-NMR (100.61 MHz): 176.41, 175.70, 175.23 (3 *s*, C(4), C(11), C(16)); 173.83, 173.57, 172.93, 172.74, 172.02, 171.77, 171.33 (7 *s*, 6 $COOCH_3$, C(9)); 163.45, 162.77 (2 *s*, C(6), C(14)); 130.4, 129.8 (2 *s*, C≡N); 103.99 (*s*, C(5)); 102.33 (*s*, C(15)); 90.32 (*d*, C(10)); 82.63 (*s*, C(1)); 74.93 (*d*, C(19)); 58.35 (*s*, C(17)); 56.67, 54.64 (2 *d*, C(3), C(8)); 53.71 (*d*, C(13)); 52.37 (*s*, C(7)); 52.37, 51.79 (3C), 51.68, 51.56 (4 *q*, 6 CH_3O); 47.08, 45.82 (2 *s*, C(2), C(12)); 46.26 (*t*, C(7^1)); 41.17 (*t*, C(2^1)); 39.33 (*d*, C(18)); 33.85, 32.60, 31.78, 31.08, 30.83, 29.78, 26.37, 25.77, 25.08 (9 *t*, 9 CH_2); 31.23 (*q*, *β*–CH_3–C(12)); 22.06, 20.72, 19.80, 18.27, 16.97 (5 *q*, 5 CH_3); 15.59 (*q*, CH_3–C(5)); 15.27 (*q*, CH_3–C(15)); –1.13 (*t*, C(7^2)). FAB-MS (glycerol): 1144 (10, $(M + 1)^+ - CN$), 1118 (16, $(M + 1)^+ - HCN–CN$), 992 (100, $(M + 1)^+ - 2CN - I$), 978 (22), 964 (43), 948 (18), 934 (23), 920 (15), 904 (15), 876 (16), 862 (18).

Hexamethyl Coα,Coβ-*Dicyano-7*^{1}*-decarboxy-7*^{1}*-methylcobyrinate* (**2**). A soln. of **1c** (250 mg) in 25 ml of MeOH containing 0.2 ml of conc. H_2SO_4 was hydrogenated (9 bar) at r.t. in the presence of 125 mg of platinum oxide hydrate (80% Pt). After 2.5 h, the catalyst was filtered off, and the soln. was diluted with 80 ml of CH_2Cl_2. The mixture was neutralized with sat. aq. $NaHCO_3$ and the org. layer was washed once with 2% aq. KCN and once with dist. H_2O. After evaporation of the solvent, **2** (200 mg, 89%) was isolated from the residue by prep. TLC using CH_2Cl_2/MeOH 96:4, to which 0.1% of KCN had been added. IR ($CHCl_3$): 2940*m*, 2920*m*, 1735*s*, 1570*m*, 1530*m*, 1390*m*, 1360*m*. UV/VIS: 582 (3.88), 542 (3.81), 505 (3.63), 418 (3.36), 368 (4.34), 352 (sh, 4.02), 314 (3.87), 306 (3.86), 277 (3.93). CD ($6.62 \cdot 10^{-5}$M): 577 (–9469), 551.5 (–3289), 536.5 (–5233), 515.5 (–2990), 449 (0), 424 (24172), 417 (23823), 395.5 (42363), 374 (0), 366 (–15450), 360 (–12709), 347 (–24421), 327 (–14952), 318.5 (–1495), 309 (–16098), 298 (–6728), 287.5 (–50), 253 (–25916), 245 (–20683), 234 (0). ^{1}H-NMR (400.13 MHz): 5.50 (*s*, H–C(10)); 3.76, 3.72, 3.70, 3.68 (6H), 3.63 (5 *s*, 6 CH_3O); 2.22 (*s*, CH_3–C(15)); 2.16 (*s*, CH_3–C(5)); 1.51, 1.67 (*q*, $J = 7.4$, CH_2 (7^1)); 1.44, 1.36, 1.34, 1.27, 1.20 (5 *s*, 6 CH_3); 0.91 (*t*, $J = 7.4$, CH_3–C(7^1)). ^{13}C-NMR (100.61

MHz): 175.85, 175.46, 175.15 (3 *s*, C(4), C(11), C(16)); 173.91, 173.77, 173.00, 172.78, 172.50, 172.08, 171.81 (7 *s*, 6 $COOCH_3$, C(9)); 165.36 (*s*, C(6)); 163.57 (*s*, C(14)); 130.5, 130.4 (2 *s*, 2 C≡N); 103.71, 101.69 (2 *s*, C(5), C(15)); 90.61 (*d*, C(10)); 82.49 (*s*, C(1)); 74.85 (*d*, C(19)); 58.26 (*s*, C(17)); 56.68 (*d*, C(3)); 54.52 (*d*, C(8)); 53.77 (*d*, C(13)); 52.30, 51.76 (2C), 51.70, 51.54 (2C) (4 *q*, 6 CH_3O); 50.51 (*s*, C(7)); 46.89 (*s*, C(12)); 45.75 (*s*, C(2)); 41.24 (*t*, $C(2^1)$); 35.38 (*d*, C(18)); 33.92, 33.43 (2 *t*, $C(3^2)$, $C(7^1)$); 32.70 (*t*, $C(17^1)$); 31.84 (*t*, $C(18^1)$); 31.20 (*t*, $C(8^2)$); 31.20 (*q*, β-CH_3–C(12)); 30.84 (*t*, $C(13^2)$); 29.79 (*t*, $C(17^2)$); 26.63 (*t*, $C(8^1)$); 25.76 (*t*, $C(13^1)$); 25.09 (*t*, $C(3^1)$); 22.06 (*q*, CH_3–C(1)); 20.09 (*q*, CH_3–C(7)); 19.83 (*q*, α–CH_3–C(12)); 18.44 (*q*, CH_3–C(17)); 16.93 (*q*, CH_3–C(2)); 15.65 (*q*, CH_3–C(5)); 15.20 (*q*, CH_3–C(15)); 8.97 (*q*, CH_3–$C(7^2)$). FAB-MS (glycerol: 1018 (45, $(M + 1)^+$–CN), 992 (100, $(M + 1)^+$–HCN–CN), 978 (49), 962 (27), 948 (16), 934 (27), 818 (33), 904 (21), 832 (34).

*Hexamethyl (6*R*)- Coα,Coβ-Dicyano-7^1-decarboxy-5-demethyl-5,6-dihydro-$6,7^1$-dimethyl-5-oxocobyrinate* (**5**). To a soln. of **2** (170 mg) in 20 ml of MeOH and 35 ml of phosphate buffer (pH 7.2), 3.25 ml of 0.01M aq. EDTA, 650 mg of ascorbic acid, and 387 mg of $KHCO_3$ were added. A gentle stream of O_2 was bubbled into the soln. at 70°. After 2 h, the mixture was treated again with 650 mg of ascorbic acid and 387 mg of $KHCO_3$ were added and heating was continued for 2 h at 80°. The cooled soln. was diluted with 30 ml of sat. aq. NaCl and extracted with CH_2Cl_2 until the org. layer became colorless. The combined org. phases were washed with 2% aq. KCN and, finally with dist. H_2O. After filtration through a cotton plug, the solvent was evaporated and the red residue purified by prep. TLC using CH_2Cl_2/MeOH 96:4 containing 0.1% of KCN to yield 55 mg of recovered **2** and 36 mg (20%) of **5**. IR: 3040*m*, 2960*m*, 2140*w*, 1735*s*, 1700*m*, 1600*m*, 1555*m*, 1410*m*, 1375*m*, 1345*m*. UV/VIS: 476 (4.10), 457 (sh, 4.03), 330 (sh, 3.86), 314 (4.16), 300 (sh, 3.94). CD ($5.95 \cdot 10^{-5}$M): 503 (13340), 489 (–47246), 454 (0), 414 (2223), 407 (0), 400 (–25013), 348 (0), 331 (39464), 317.5 (81152), 306 (0), 288 (–27236), 275 (0), 271.5 (6114), 267.5 (0), 257.5 (–7226), 240.5 (–2223°). ^{1}H-NMR (400.13 MHz): 5.13 (*s*, H–C(10)); 3.76, 3.73, 3.71 (6H), 3.68, 3.64 (5 *s*, 6 CH_3O)); 2.15 (*s*, CH_3–C(15)); 1.67 (*s*, CH_3–C(1)); 1.55 (*s*, CH_3–C(6)); 1.33 (*s*, CH_3–C(2)); 1.31 (*s*, CH_3–C(7)); 1.29 (*s*, α–CH_3–C(12)); 1.22 (*s*, CH_3–C(17)); 1.14 (*s*, β–CH_3–C(12)); 0.83 (*t*, CH_3–$C(7^1)$). ^{13}C-NMR (100.61 MHz): 194.21 (*s*, C(5)); 175.87, 174.01, 173.95, 173.64, 173.08, 173.05, 172.81, 171.72, 171.37, 171.12 (10 *s*, 6 $COOCH_3$, C(11), C(4), C(16), C(9)); 166.13 (*s*, C(14)); 131.84, 130.67 (2 *s*, 2 C≡N); 97.78 (*s*, C(15)); 89.39 (*d*, C(10)); 88.00, 82.53 (2*s*, C(1), C(6)); 74.20 (*d*, C(19)); 57.85 (*s*, C(17)); 55.79, 54.33, 54.27 (3 *d*, C(3), C(8), C(13)); 52.37, 51.86, 51.80, 51.75 (2C), 51.56 (5 *q*, 6 CH_3O); 49.38 (*s*, C(7)); 46.14 (*s*, 2C, C(2), C(12)); 41.11 (*t*, C(2)); 39.89 (*d*, C(18)); 33.73, 33.60, 33.27, 31.90, 31.01, 29.96 (2C), 26.71, 25.66, 24.26 (9 *t*, 10 CH_2); 29.96 (*q*, β–CH_3–C(12)); 25.66 (*q*, CH_3–C(6)); 21.45 (*q*, CH_3–C(1)); 20.23 (*q*, α–CH_3–C(12)); 19.05 (*q*, CH_3–C(17)); 16.62 (*q*, CH_3–C(2)); 16.31 (*q*, CH_3–C(7)); 14.41 (*q*, CH_3–C(15)); 9.49 (*q*, CH_3–$C(7^1)$). FAB-MS (glycerol): 1009 (100, $(M + 1)^+$–2CN), 995 (20), 993 (18),979 (16), 977 (14), 951 (16), 949 (16), 935 (17), 921 (15), 907 (16).

Coα,Coβ-Dicyano-2,7,18-tris(2-hydroxyethyl)-3,8,13,17-tetrakis(3-hydroxypropyl)-1,2,5,7,12,12,15,17-octamethylcobalticorrin (**6a**). A soln. of heptamethyl Coα,Coβ-dicyanocobyrinate (1 g) in CH_2Cl_2 (40 ml) was treated with 10 ml of 30% aq. $HClO_4$. After *ca.* 3 min, the color had changed from violet to light red, and the liberated HCN was evaporated. The org. layer was separated, washed twice with dist. H_2O and dried by filtration through a cotton plug. The solvent was evaporated and the product dried in vacuo over P_4O_{10} for 24 h. The obtained heptamethyl aquocyanocobyrinate was dissolved in 25 ml of freshly distilled dry THF and the soln. added dropwise during 1 h under vigorous stirring to a cooled (0°) suspension of $LiAlH_4$ (800 mg) in 170 ml of dry THF. Stirring of the grey-green mixture was continued for 3 h at 0°. Thereafter, the soln. was poured into 200 g of ice/H_2O, acidified with HCl (1N), concentrated under reduced pressure to 100 ml and transferred to a short *XAD* column (50 g; *Serva*, D-6900 Heidelberg). The inorg. salts were eluted first with dist. H_2O, then the column was washed with 1% aq. HCN, and finally with dist. H_2O until the eluate was neutral. The product was eluted with MeOH, and after removing of the solvent, the residue was further purified by column chromatography on DEAE-cellulose (*Macherey-Nagel & Co.*, D-5160 Düren) using dist. H_2O. After evaporation, the residue was dried over P_4O_{10} for 48 h to yield 780 mg (95%) of **6a** as a violet powder. IR (KBr): 3370, 2910, 2860, 2120, 1660, 1630, 1590, 1505, 1410, 1375. UV/VIS: 581, 542, 510 (sh), 418, 368, 353 (sh), 313, 308, 277, 217. ^{1}H-NMR (100 MHz, CD_3OD): 5.66 (*s*, H–C(10)); 2.7 (*m*, H–C(18)); 2.32, 2.26 (2 *s*, CH_3–C(5), CH_3–C(15)); 1.56, 1.40 (9H), 1.29, 1.16 (4 *s*, 6 CH_3).

Coα,Coβ-Dicyano-$7^1,7^2$-dihydro-2,18-bis(2-hydroxyethyl)-3,8,13,17-tetrakis(3-hydroxypropyl)-1,2,5,7,12,12,15,17-octamethylfuro[3,2-g]cobalticorrin (**7a**). *i*) From heptamethyl aquocyanocobyrinate following the method of preparation of **6a**. Excess $LiAlH_4$ was removed by hydrolysis. Then the mixture was allowed to stand at r.t. overnight. Workup as described before afforded **7a** (775 mg, 95%).

ii) From **6a** (10 mg) by reaction with 5 ml of aq. KOH (5%) for 3 h at r.t. After neutralisation with HCl (1N), the corrinoids were adsorbed on *XAD*, washed with dist. H_2O and eluted with MeOH to yield 10 mg of **7a**. IR (KBr): 3370, 2910, 2860, 2120, 1660, 1630, 1540, 1505, 1410, 1375. UV/VIS: 583, 544, 512 (sh), 416, 367, 351 (sh),

314.5, 304.5, 277.5, 215. ^{1}H-NMR (100 MHz, CD_3OD): 5.74 (*s*, H–C(10)); 3.09 (*m*, H–C(3), H–C(13)); 2.68 (*m*, H–C(18)); 2.35 (*s*, CH_3–C(5), CH_3–C(15)); 1.63, 1.50, 1.43 (6H), 1.31, 1.16 (5 *s*, 6 CH_3)).

Coα,Coβ-*Dicyano-2,7,18-tris(2-acetoxyethyl)-3,8,13,17-tetrakis(3-acetoxypropyl)-1,2,5,7,12,12,15,17-octamethylcobalticorrin* (**6b**). To a ice-cooled soln. of **6a** (150 mg) in 20 ml of dry THF, 0.59 ml of dry pyridine were added under N_2. After injection of 0.8 ml of AcCl through a rubber septum, the mixture was kept at 0° for 3 h and then allowed to reach r.t. After dilution with 20 ml of CH_2Cl_2, the soln. was washed successively with distilled H_2O, 2% aq. KCN and again with dist. H_2O. The org. layer was separated and dried by filtration through a cotton plug. Purification of the crude product by prep. TLC using CH_2Cl_2/MeOH 97.5:2.5, to which 0.1% of KCN had been added, yielded 142 mg (71%) of **6b**. IR ($CHCl_3$): 2990, 2950, 2880, 2130, 1740, 1590, 1510, 1480, 1410, 1395, 1375. UV/VIS: 581 (3.97), 542 (3.92), 510 (sh), 418 (3.31), 368 (4.48), 353 (sh), 313 (3.92), 308 (3.92), 277 (4.01), 217 (4.66). ^{1}H-NMR (100 MHz): 5.49 (*s*, H–C(10)); 3.9–4.5 (*m*, H–C(19), 7 CH_2O); 3.1 (1H), 2.90 (2H) (2 *m*, H–C(3), H–C(8), H–C(13)); 2.23, 2.18 (2 *s*, CH_3–C(5), CH_3–C(15)); 2.11, 2.08, 2.07, 2.06, 2.03, 2.02, 2.00 (7 *s*, 7 CH_3COO); 2.3–1.6 (*m*, H–C(18), CH_2); 1.46 (6H), 1.35, 1.30 (6H), 1.19 (4 *s*, 6 CH_3). ^{13}C-NMR (25.16 MHz): 176.2, 176.1, 174.9 (3 *s*, C(4), C(11), C(16)); 171.7, 170.8 (6C), 170.5 (3 *s*, 7 CH_3COO, C(9)); 164.0, 163.6 (2 *s*, C(6), C(14)); 102.9, 101.7 (2 *s*, C(5), C(15)); 90.3 (*d*, C(10)); 82.8 (*s*, C(1)); 75.5 (*d*, C(19)); 64.5, 64.3, 63.9, 63.8 (4 *t*, $C(3^3)$, $C(8^3)$, $C(13^3)$, $C(17^3)$); 62.1, 61.4 (2 *t*, $C(2^2)$, $C(18^2)$); 60.9 (*t*, $C(7^2)$); 58.1 (*s*, C(17)); 58.1 (*d*, C(3)); 55.8 (*d*, C(8)); 54.4 (*d*, C(13)); 48.5 (*s*, C(7)); 46.8, 45.9 (2 *s*, C(2), C(12)); 39.1 (*d*, C(18)); 38.3 (*t*, $C(7^1)$); 35.5, 35.2, 29.6, 28.0, 27.0, 26.5, 26.2 (2C), 25.9, 24.4 (9 *t*, 10 CH_2); 31.3 (*q*, β–CH_3–C(12)); 20.9, 20.8 (2 *q*, 7 CH_3COO); 22.4, 20.1, 19.7, 18.6, 16.5, 15.6, 15.2 (7 *q*, 7 CH_3).

Coα,Coβ-*Dicyano-2,18-bis(2-acetoxyethyl)-3,8,13,17-tetrakis(3-acetoxypropyl)-7^1,7^2-dihydro-1,2,5,7,12,12,15,17-octamethylfuro[3,2-g]cobalticorrin* (**7b**). According to the method described for **6b**, 138 mg (72%) of **7b** were obtained from 150 mg of **7a**. IR ($CHCl_3$): 2990, 2950, 2880, 2130, 1740, 1590, 1510, 1480, 1410, 1395, 1375. UV/VIS: 583 (3.91), 544 (3.91), 512 (sh), 416 (3.37), 367 (4.45), 351 (sh), 314.5 (3.92), 304.5 (3.88), 277.5 (3.93), 216 (4.78). ^{1}H-NMR (100 MHz): 5.67 (*s*, H–C(10)); 4.4–3.8, 3.5 (2 *m*, 7 CH_2O); 3.13, 2.97 (2 *m*, H–C(3), H–C(13)); 2.23 (*s*, CH_3–C(5), CH_3–C(15)); 2.12, 2.09, 2.07, 2.05, 2.00 (6H) (5 *s*, 6 CH_3COO); 2.5–1.6 (H–C(18), CH_2); 1.56, 1.48, 1.39, 1.30 (6H), 1.21 (5 *s*, 6 CH_3). ^{13}C-NMR (25.16 MHz): 177.7, 176.2, 174.9 (3 *s*, C(4), C(11), C(16)); 170.9 (6C), 170.6 (2 *s*, 6 CH_3COO, C(9)); 163.8, 163.5 (2 *s*, C(6), C(14)); 130.3, 129.8 (2 *s*, 2 C≡N); 102.5, 102.0 (2 *s*, C(5), C(15)); 95.3 (*s*, C(8)); 87.7 (*d*, C(10)); 82.9 (*s*, C(1)); 75.8 (*d*, C(19)); 66.0 (*t*, $C(7^2)$); 64.5 (2C), 64.0, 63.8 (3 *t*, $C(3^3)$, $C(8^3)$, $C(13^3)$, $C(17^3)$); 62.1, 61.5 (2 *t*, $C(2^2)$, $C(18^2)$); 58.1 (*s*, C(17)); 58.1 (*d*, C(3)); 54.7 (*d*, C(13)); 53.1 (*s*, C(7)); 47.1, 45.9 (2 *s*, C(2), C(12)); 43.0 (*t*, $C(7^1)$); 39.2 (*d*, C(18)); 35.8, 35.2, 31.4, 29.7, 27.1, 26.7, 26.2, 25.9, 24.5, 23.0 (10 *t*, 10 CH_2); 31.0 (*q*, β–CH_3–C(12)); 22.4, 21.0, 20.8, (6C), 19.7, 18.8, 16.9, 16.5 (7 *q*, 6 CH_3COO, 6 CH_3); 15.2 (*q*, CH_3–C(15)).

Coα,Coβ-*Dicyano-2,7,18-tris(2-(methanesulfonyloxyethyl)-3,8,13,17-tetrakis(3-(methanesulfonyloxypropyl)-1,2,5,7,12,12,15,17-octamethylcobalticorrin* (**6c**). To a soln. of carefully dried **6a** (780 mg) in 80 ml of dry DMF, 1.95 ml of dry Et_3N and 0.6 ml of MsCl were added under N_2 at − 5° during 10 min. The mixture was allowed to reach r.t. (4–5 h), and stirring was continued for 20 h. Then, the soln. was treated with 2 ml of MeOH to remove the excess MsCl. The solvent was evaporated (50°/0.1 Torr) and the residue dissolved in *ca.* 20 ml of CH_2Cl_2 was washed successively with dist. H_2O, 1% aq. HCN, and again with H_2O. The org. phase was dried by filtration through a cotton plug and the solvent evaporated. The product was isolated by column chromatography (70 g of silica gel containing 50 mg of KCN) using CH_2Cl_2/MeOH 97:3 and recrystallized from CH_2Cl_2/MeOH to yield 767 mg (61%) of **6c** as dark-red needles of m.p. 146–148° (dec.). IR ($CHCl_3$): 3020, 3000, 2970, 2930, 2105, 1578, 1498, 1395, 1355, 1185. UV/VIS: 585 (3.92), 543 (3.91), 510 (sh), 419 (3.45), 370 (4.42), 356 (sh), 316 (3.98), 278.5 (4.07). ^{1}H-NMR (100 MHz): 5.55 (*s*, H–C(10)); 4.7–3.8 (*m*, 7 CH_2O); 3.90 (*d*, J = 10, H–C(19)); 3.09, 3.05, 3.04, 3.03, 2.97, 2.96, 2.93 (7 *s*, 7 CH_3SO_3); 2.26, 2.22 (2 *s*, CH_3–C(5), CH_3–C(15)); 2.4–1.6 (*m*, H–C(18), CH_2); 1.57, 1.49, 1.40 (6H), 1.33, 1.22 (5 *s*, 6 CH_3). ^{13}C-NMR (25.16 MHz): 177.0, 176.3, 175.0 (3 *s*, C(4), C(11), C(16)); 171.7 (*s*, C(9)); 163.4, 162.9 (2 *s*, C(6), C(14)); 135 (*s*, 2 C≡N); 103.5 (*s*, C(5)); 102.4 (*s*, C(15)); 90.0 (*d*, C(10)); 82.7 (*s*, C(1)); 75.7 (*d*, C(19)); 70.9, 70.4, 70.3, 69.2 (4 *t*, $C(3^3)$, $C(8^3)$, $C(13^3)$, $C(17^3)$); 67.5 (2C), 67.3 (2 *t*, $C(2^2)$, $C(7^2)$, $C(18^2)$); 58.0 (*s*, C(17)); 58.0 (*d*, C(3)); 56.6 (*d*, C(8)); 54.1 (*d*, C(13)); 48.5 (*s*, C(7)); 46.8, 46.5 (2 *s*, C(2), C(12)); 38.6, 37.9, 37.6, 37.3 (4 *q*, 7 CH_3SO_3); 35.1 (*d*, C(18)); 41.2, 30.2, 28.0, 27.6, 26.2, 25.9, 25.1 (7 *t*, 11 CH_2); 31.5 (*q*, β–CH_3–C(12)); 22.9, 21.5, 19.6, 18.4 (2C) (4 *q*, 5 CH_3); 15.6 (*q*, CH_3–C(5)); 15.4 (*q*, CH_3–C(15)). Anal. calc. for $C_{54}H_{87}CoN_6O_{21}S_7$ (1439.7): C 45.05, H 6.09, N 5.84, O 23.34, S 15.59; found: C 45.11, H 6.10, N 5.96, O 24.22, S 14.80.

Coα,Coβ-*Dicyano-7^1,7^2-dihydro-2,18-bis(2-(methanesulfonyloxy)ethyl)-3,8,13,17-tetrakis(3-(methanesulfonyloxy)propyl)-1,2,5,7,12,12,15,17-octamethylfuro[3,2-g]cobalticorrin* (**7c**). Following the method described for **6c**, **7c** (764 mg, 64%) was obtained from **7a** (775 mg) as dark-red needles of m.p. 124–125°. IR ($CHCl_3$): 3010, 2970, 2110, 1580, 1498, 1395, 1355, 1185. UV/VIS: 584 (3.94), 544 (3.93), 512 (sh), 417 (3.46), 369 (4.44), 355 (sh), 315 (4.06), 304.5 (3.98), 277.5 (4.09). ^{1}H-NMR (100 MHz): 5.71 (*s*, H–C(10)); 3.88 (*d*, J = 10, H–C(19)); 4.7–4.0, 3.49

(*m*, 7 CH_2O); 3.09, 3.06, 3.03 (6H), 2.96 (6H) (4 *s*, 6 CH_3SO_3); 2.3–1.8 (*m*, CH_2); 2.51 (*s*, CH_3–C(5), CH_3–C(15)); 1.58, 1.50, 1.34, 1.20 (4 *s*, 4 CH_3). Anal. calc. for $C_{54}H_{83}CoN_6O_{19}S_6$ (1371.6): C 47.29, H 6.10, N 6.13, O 22.16, S 14.02; found: C 46.75, H 6.25, N 5.93, O 23.55, S 14.39.

Co*α*,Co*β*-*Dicyano-2,7,18-triethyl-1,2,5,7,12,12,15,17-octamethyl-3,8,13,17-tetrapropyl-cobalticorrin* (**6d**). To a stirred soln. of **6c** (767 mg) in dry THF (75 ml), 0.1M Li(Et_3BH) in THF[8]) (28 ml) was added under N_2 at 0°. After warming to r.t., stirring was continued in the darkness for 60 h. Then, 40 ml of MeOH and KCN (550 mg) were added, and the vigorously stirred mixture was irradiated with a 500-watt W-lamp under O_2 at 0° until the UV/VIS showed only the characteristic bands of the dicyano-Co(III) complex. The mixture was then diluted with CH_2Cl_2 (100 ml) and shaken repeatedly with dist. H_2O. The org. phase was separated, dried by filtration through a cotton plug, and the solvent evaporated. The residue was purified by prep. TLC using CH_2Cl_2/MeOH 99.5:0.5 which contained 0.1% of KCN. After crystallisation from Et_2O/hexane, 278 mg (67%) of **6d** were obtained, m.p. 204° (dec.). IR ($CHCl_3$): 2960, 2870, 2110, 1615, 1580, 1498, 1470, 1455, 1395, 1375, 1360. UV/VIS: 588 (4.03), 538 (3.96), 504 (sh), 417 (3.43), 368 (4.51), 350 (sh), 312 (3.91), 276.5 (4.08), 213 (4.90). CD: 603 (0), 570.5 (−21600), 548 (−11100), 532.5 (−15900), 462 (0), 421.5 (36500), 412 (33700), 393 (49100), 368 (0), 361 (−15000), 357.5 (−14100), 343.5 (−29300), 326.5 (−14100), 321.5 (−15900), 315 (−6600), 305 (−23350), 289.5 (0), 276 (6300). ^{1}H-NMR (100 MHz): 5.40 (*s*, H–C(10)); 3.86 (*d*, *J* = 10, H–C(19)); 2.65–3.0 (*m*, H–C(3), H–C(8), H–C(13)); 2.16, 2.11 (2 *s*, CH_3–C(5), CH_3–C(15)); 2.0–1.3 (*m*, 11 CH_2); 1.43, 1.37, 1.32, 1.22, 1.18 (6H) (5 *s*, 6 CH_3); 1.1–0.8 (*m*, 7 CH_3 of Et and Pr). ^{13}C-NMR (25.16 MHz): 176.5, 175.3, 175.1 (3 *s*, C(4), C(11), C(16)); 172.6 (*s*, C(9)); 164.5, 163.7 (2 *s*, C(6), C(14)); 102.6, 101.1 (2 *s*, C(5), C(15)); 89.5 (*d*, C(10)); 82.8 (*s*, C(1)); 76.0 (*d*, C(19)); 58.6 (*s*, C(17)); 56.9 (*d*, C(3)); 54.8 (*d*, C(8)); 55.0 (*d*, C(13)); 50.0 (*s*, C(7)); 46.7, 46.4 (2 *s*, C(2), C(12)); 44.3 (*d*, C(18)); 42.0 (*t*, $C(17^1)$); 33.5, 33.2, 33.1, 31.8 (4 *t*, $C(3^1)$, $C(7^1)$, $C(8^1)$, $C(13^1)$); 28.4 (*t*, $C(2^1)$); 23.8 (*t*, $C(3^2)$); 21.0, 20.9, 20.8 (3 *t*, $C(8^2)$, $C(13^2)$, $C(18^1)$); 18.3 (*t*, $C(17^2)$; 31.2 (*q*, *β*–CH_3–C(12)); 22.5 (*q*, CH_3–C(1)); 20.1, 19.9 (2 *q*, *α*–CH_3–C(12), CH_3–C(7)); 18.2 (*q*, CH_3–C(17)); 15.3 (*q*, CH_3–C(2)); 15.5 (*q*, CH_3–C(5)); 15.1 (*q*, CH_3–C(15)); 14.5, 14.4, 14.3, 14.2, 13.7 (5 *q*, $C(3^3)$, $C(8^3)$, $C(13^3)$, $C(17^3)$, $C(18^2)$); 9.3, 8.9 (2 *q*, $C(2^2)$, $C(7^2)$). EI-MS: 780 (2, M^+), 765 (0.4), 751 (33), 728 (100, M^+–2CN), 727 (86), 726 (92), 698 (84), 684 (9), 375.5 (2), 363.5 (14), 348.5 (9), 342.5 (9). Anal. calc. for $C_{47}H_{73}CoN_6$ (781.1): C 72.28, H 9.42, N 10.76; found: C 72.30, H 9.43, N 10.86.

Co*α*,Co*β*-*Dicyano-2,18-diethyl-7^1,7^2-dihydro-1,2,5,7,12,12,15,17-octamethyl-3,8,13,17-tetrapropylfuro[3,2-g]cobalticorrin* (**7d**) was prepared from **7c** (764 mg) following the procedure described above for **6d**. After crystallisation from Et_2O/hexane, 310 mg (70%) were obtained, m.p. 115° (dec.). IR ($CHCl_3$): 2960, 2950, 2865, 2110, 1580, 1500, 1470, 1398, 1360. UV/VIS: 581 (3.99), 541 (3.94), 510 (sh), 413 (3.37), 3.64 (4.47), 350 (sh), 313 (3.94), 302 (3.91), 276 (3.97). CD: 576 (−21300), 555 (−11700), 538 (−15900), 485 (0), 417 (29300), 412 (28600), 389 (42900), 372 (sh, 22000), 363 (0), 357 (sh, −11400), 344 (−26400), 326 (0), 320.5 (6600), 316 (0), 309 (sh, −11400), 301.5 (−16900), 286 (−3100), 276 (−10300), 266 (−4800), 249 (−24900), 243 (−19100°). ^{1}H-NMR (100 MHz): 5.61 (*s*, H–C(10)); 3.83 (*d*, *J* = 10, H–C(19)); 3.85, 3.46 (2 *m*, $CH_2(7^2)$); 2.96, 2.80 (2 *m*, H–C(3), H–C(13)); 2.55–1.6 (*m*, CH_2); 2.19 (*s*, CH_3–C(5), CH_3–C(15)); 1.53, 1.47, 1.35, 1.23, 1.19 (6H) (5 *s*, 6 CH_3), 1.15–0.8 (*m*, 6 CH_3 of Et and Pr). ^{13}C-NMR (25.16 MHz): 177.2, 176.9, 175.3 (3 *s*, C(4), C(11), C(16)); 170.7 (*s*, C(9)); 163.7, 162.7 (2 *s*, C(6), C(14)); 102.4, 102.0 (2 *s*, C(5), C(15)); 95.4 (*s*, C(8)); 87.3 (*d*, C(10)); 83.0 (*s*, C(1)); 76.3 (*d*, C(19)); 65.8 (*t*, $C(7^2)$); 58.7 (*s*, C(17)); 57.0 (*d*, C(3)); 55.0 (*d*, C(13)); 53.0 (*s*, C(7)); 47.2, 46.6 (2 *s*, C(2), C(12)); 44.5 (*d*, C(18)); 42.2 (*t*, $C(17^1)$); 42.9, 37.2, 33.2, 31.7 (4 *t*, $C(3^1)$, $C(7^1)$, $C(8^1)$, $C(13^1)$); 28.4 (*t*, $C(2^1)$); 23.8 (*t*, $C(3^2)$); 21.2, 20.8, 17.0 (3 *t*, $C(8^2)$, $C(13^2)$, $C(18^1)$); 18.4 (*t*, $C(17^2)$); 30.9 (*q*, *β*–CH_3–C(12)); 22.6 (*q*, CH_3–C(1)); 20.8, 19.9 (2 *q*, *α*–CH_3–C(12), CH_3C(7)); 18.4 (*q*, CH_3–C(17)); 15.3 (*q*, CH_3–C(2)); 17.1 (*q*, CH_3–C(5)); 15.2 (*q*, CH_3–C(15)); 14.9, 14.5, 14.4, 14.2, 13.7 (5 *q*, $C(3^3)$, $C(8^3)$, $C(13^3)$, $C(17^3)$, $C(18^2)$); 9.3 (*q*, $C(2^2)$). EI-MS: 794 (1, M^+), 742 (8, M^+–2CN), 740 (2), 712 (1), 698 (89), 349 (4), 334.5 (2), 327.5 (2), 207 (10), 205 (10), 71 (20), 58 (100). Anal. calc. for $C_{47}H_{71}CoN_6O$: C 71.00, H 9.00, N 10.57, O 2.01; found: C 71.08, H 9.12, N 10.48, O 2.04.

Co*α*,Co*β*-*Dicyano-2,7,18-triethyl-5,6-dihydro-1,2,6,7,12,12,15,17-octamethyl-5-oxo-3,8,13,17-tetrapropylcobalticorrin* (**12**). A gentle stream of O_2 was bubbled at 80° into a soln. of **6d** (300 mg), ascorbic acid (2.8 g), and $KHCO_3$ (1.57 g) in MeOH (210 ml) containing 70 ml of phosphate buffer (pH 7.2) and 7 ml of aq. EDTA soln. (0.01M). After 2 h, ascorbic acid (2.8 g) and $KHCO_3$ (1.57 g) were added, and the reaction was continued for 2 h. The mixture was cooled, diluted with H_2O and extracted with CH_2Cl_2 until the org. layer stayed colorless. After addition of aq. HCN (1%), the combined org. phases were dried by filtration through a cotton plug, and the solvent was evaporated. From the residue, 87 mg (29%) of **12**, 52 mg (17%) of **6d** as well as 26 mg (9%) of an uncharacterized red by-product were isolated by prep. TLC using CH_2Cl_2/MeOH 99.5:0.5, which contained 0.1% of KCN. Recrystallization from CH_2Cl_2/hexane afforded yellow crystalls of **12**, m.p. 225° (dec.). IR ($CHCl_3$): 2960, 2925, 2865, 2110, 1690, 1592, 1545, 1485, 1460, 1410, 1380. UV/VIS: 472 (4.08), 460 (sh), 314 (4.16), 302 (sh), 229 (sh),

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[8]) 'Superhydride' (*Aldrich-Chemie*, D-7924 Steinheim).

215 (4.64). CD: 498 (18200), 483 (0), 450 (−50000), 414 (0), 403 (9500), 392 (0), 370 (−21600), 347 (0), 326 (sh, 44200), 313 (88100), 296 (0), 284.5 (−25300), 274 (0), 267.5 (7900), 263.5 (0). ^{1}H-NMR (100 MHz): 5.00 (*s*, H−C(10)); 3.98 (*d*, *J* = 10, H−C(19)); 3.25, 2.64 (2H) (2 *m*, H−C(3), H−C(8), H−C(13)); 2.30 (*m*, H−C(18)); 2.12 (*s*, CH_3−C(15)); 2.0–1.4 (*m*, 11 CH_2); 1.61, 1.54, 1.30, 1.26, 1.23, 1.19, 1.14 (7 *s*, 7 CH_3); 1.05–0.85 (*m*, 7 CH_3 of Et and Pr). ^{13}C-NMR (25.16 MHz): 195.0 (*s*, C(5)); 176.0, 175.4, 174.0, 171.1 (4 *s*, C(4), C(9), C(11), C(16)); 166.0 (*s*, C(14)); 97.2 (*s*, C(15)); 88.4 (*s*, C(1)); 88.4 (*d*, C(10); 82.2 (*s*, C(6)); 75.2 (*d*, C(19)); 58.4 (*s*, C(17)); 55.4, 55.0 (2C) (2 *d*, C(3), C(8), C(13)); 49.0 (*s*, C(7)); 47.1, 46.0 (2 *s*, C(2), C(12)); 44.8 (*d*, C(18)); 42.5 (*t*, C(17^1)); 33.9, 33.0, 30,9, 29.7 (4 *t*, C(3^1), C(7^1), C(8^1), C(13^1)); 28.4 (*t*, C(2^1)); 23.2 (2C), 21.3, 21.0, 18.4 (4 *t*, C(3^2), C(13^2), C(17^2), C(18^1)); 30.0 (*q*, *β*−CH_3−C(12)); 25.3 (*q*, CH_3−C(6)); 21.9 (*q*, CH_3−C(1)); 20.2, 18.6, 16.2, 15.1, 14.6, 14.5 (2C), 14.1, 13.9, 13.6 (9 *q*, CH_3−C(2), CH_3−C(7), α−CH_3−C(12), CH_3−C(15), CH_3−C(17), C(3^3), C(8^3), C(13^3), C(17^3), C(18^2)); 8.8 (*q*, C(2^2)); 9.4 (*q*, C(7^2)). EI-MS: 796 (6, M^+), 769 (10), 744 (100, M^+ −2CN), 714 (10), 317 (4). Anal. calc. for $C_{47}H_{73}CoN_6O$ (797.0): C 70.83, H 9.23, N 10.54; found: C 70.15, H 8.99, N 10.02.

Coα,Coβ-*Dicyano-2,18-diethyl-5,6,7^1,7^2-tetrahydro-1,2,6,7,12,12,15,17-octamethyl-5-oxo-3,8,13,17-tetrapropylfuro[3,2-g]cobalticorrin* (**13**). A gentle stream of O_2 was bubbled at 70° into a soln. of **7d** (240 mg), ascorbic acid (1.45 g), and $KHCO_3$ (1.1 g) in 150 ml of MeOH containing 30 ml of phosphate buffer (pH 7.2) and 5 ml of aq. EDTA soln. (0.01M). Ascorbic acid (2.9 g) and $KHCO_3$ (2.2 g) were added in 2 aliquot portions after 2 and 4 h, and subsequently, the reaction was continued for 2 h more. Thereafter, the mixture was worked up as described for **12** to yield 45 mg (19%) of **13**, 105 mg (44%) of **7d**, and 14 mg (6%) of an uncharacterized red by-product. After recrystallization from CH_2Cl_2/hexane, yellow crystalls of **13**, m.p. 198° (dec.), were obtained. IR ($CHCl_3$): 2990, 2925, 2870, 2110, 1715, 1695, 1585, 1542, 1460, 1405, 1380. UV/VIS: 468 (4.07), 330 (sh), 314 (4.16), 302 (sh), 216 (4.64). CD: 570 (7000), 529 (5900), 509 (6400), 491.5 (0), 450 (−43100), 407.5 (0), 401 (2400), 395.5 (sh, 1100), 393 (0), 376 (−14300), 371 (−15700), 351 (0), 329 (49800), 313 (116400), 295.5 (0), 286 (−24200), 273.5 (0), 286 (−24200), 273.5 (0), 271 (4600), 286 (0), 256 (−29700). ^{1}H-NMR (100 MHz): 5.17 (*s*, H−C(10)); 3.93 (*d*, *J* = 10, H−C(19)); 3.86 (*t*, *J* = 7, CH_2(7^2)); 3.36, 2.68 (2 *m*, H−C(3), H−C(13)); 2.35 (*m*, H−C(18)); 2.11 (*s*, CH_3−C(15)); 2.09 (*t*, *J* = 7, CH_2(7^1)); 2.0–1.2 (*m*, 10 CH_2); 1.63, 1.51, 1.34, 1.23, 1.20, 1.16, 1.10 (7 *s*, 7 CH_3); 1.0–0.9 (*m*, 6 CH_3 of Et and Pr). ^{13}C-NMR (25.16 MHz): 194.9 (*s*, C(5)); 176.6, 175.6, 174.1, 172.1 (4 *s*, C(4), C(9), C(11), C(16)); 166.0 (*s*, C(14)); 97.7 (*s*, C(15)); 94.3 (*s*, C(8)); 88.3 (*s*, C(1)); 87.2 (*d*, C(10)); 80.1 (*s*, C(6)); 75.4 (*d*, C(19)); 66.4 (*t*, C(7^2)); 58.4 (*s*, C(17)); 55.6 (*d*, C(3)); 54.7 (*d*, C(13)); 55.1 (*s*, C(7)); 47.7, 46.2 (2 *s*, C(2), C(12)); 44.9 (*d*, C(18)); 42.6 (*t*, C(17^1)); 40.9 (*t*, C(7^1)); 37.8 (*t*, C(8^1)); 33.1, 31.1 (2 *t*, C(3^1), C(13^1)); 28.6 (*t*, C(2^1)); 22.9, 21.4, 20.9, 18.5, 17.9 (5*t*, C(3^2), C(8^2), C(13^2), C(17^2), C(18^1)); 30.0 (*q*, *β*−CH_3−C(12)); 22.3 (*q*, CH_3−C(6)); 21.9 (*q*, CH_3−C(1)); 20,2, 18.7, 17.5, 15.4, 15.0, 14.7 (2C), 14.6, 14.0, 13.7 (9 *q*, CH_3−C(2), CH_3−C(7), α−CH_3−C(12), CH_3−C(15), CH_3−C(17), C(3^3), C(8^3), C (13^3), C(17^3), C(18^2)); 8.8 (*q*, C(2^2)). EI-MS: 810 (7, M^+), 703 (3), 758 (47, M^+ − 2CN), 756 (27), 755 (30), 728 (12), 349 (10), 250 (8), 208 (7), 182 (6), 168 (7), 150 (15), 112 (15), 111 (14), 97 (12), 83 (18), 71 (44), 58 (100).

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