116. A Lipophilic Derivative of Vitamin B_{12} as a Selective Carrier for Anions

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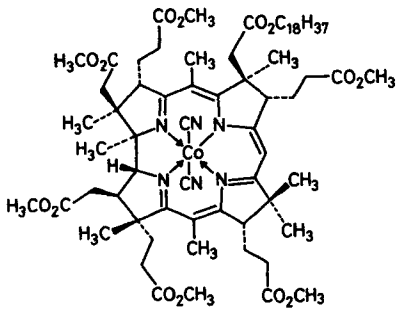
(21.III.84)

Summary

Incorporation of the lipophilic Co(III)-cobyrinate octadecyl-cobester **1** and of its ionic aqua-cyano perchlorate derivative **2** into poly(vinyl chloride)/bis(1-butylpentyl) adipate liquid membranes induces a selectivity, measured potentiometrically, of about 10^3 for SCN^- and NO_2^- with respect to Cl^-, but only of about 4 for ClO_4^- *vs.* Cl^-. This is in contrast to classical anion-exchanger membranes, which exhibit a selectivity sequence $ClO_4^- > SCN^- \gg NO_2^- > Cl^-$ in accordance with the *Hofmeister* series. The Co(III)-corrins **1** and **2**, when components in solvent polymeric membranes, undergo exchange of axial ligands and behave as highly selective carriers for SCN^- and NO_2^-.

An anion-selectivity sequence with a preference for lipophilic and a rejection of hydrophilic anions [1] is characteristic of liquid membranes based on various classical anion exchangers [2] such as quarternary ammonium salts or metal-phenanthrolinates (*Hofmeister* series [3]). For dissociated anion exchangers, where the complexation between the cationic sites and the counterions is negligible, the anion selectivity is controlled by the distribution coefficients of the anions between the aqueous sample phase and the membrane phase [1][4]. A different behaviour is expected for associated anion exchangers. In this case, the parameters determining the selectivity strongly depend on the stability constants of the complexes of the exchanger sites with the counterions, provided that the mobilities of these sites are large compared to those of the counterions [1][4]. During our search for components with a selective interaction between cationic sites and counterions, vitamin B_{12} and its derivatives appeared as promising candidates. This was supported by the available information on their complexation behaviour towards anionic ligands in aqueous solutions [5]. For exploratory potentiometric studies on anion-selective properties of vitamin B_{12} derivatives in membranes, the lipophilic Co(III)-complex **1** was prepared. This was followed by the synthesis of **2** and **3**, which were used for an evaluation of structural effects and for comparison with *Rétey*'s cholestano-cobaloxime **4** (chlorobis(cholestane-2,3-dione dioxime)pyridine-cobalt) [6] and the quarternary ammonium salt **5** [7]. The lipophilic Co(III)-cobyrinate octadecyl-cobester **1** (*a,b,d,e,f,g*-hexamethyl *c*-octadecyl *Coα,Coβ*-dicyanocobyrinate) was prepared by a sequence of four steps from vitamin B_{12} *via* vitamin-B_{12}-*c*-lactone (*Coα*-[α-(5,6-dimethylbenzimidazolyl)]-*Coβ*-cyanocobamic acid *a,b,d,e,g*-pentaamide

Scheme



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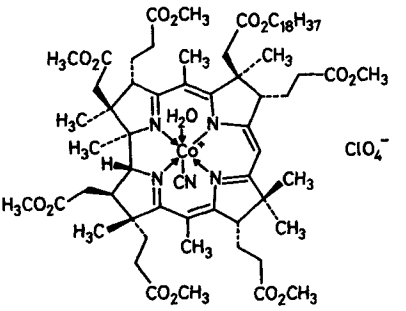
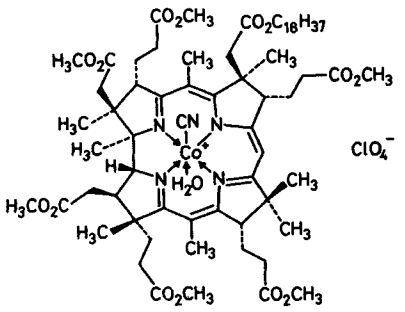


2a



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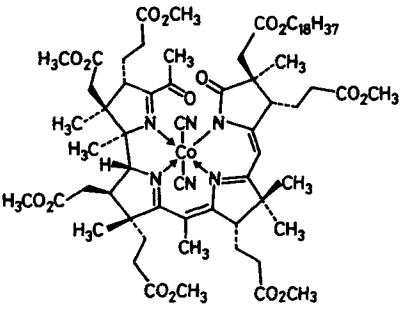

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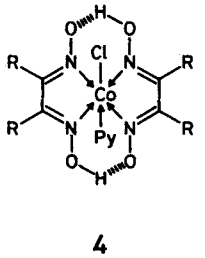

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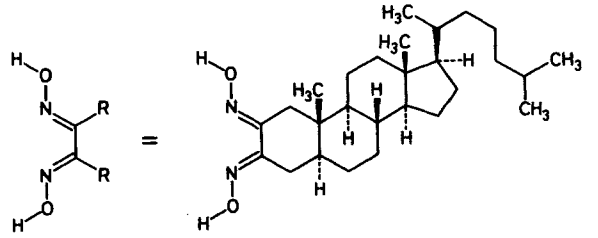

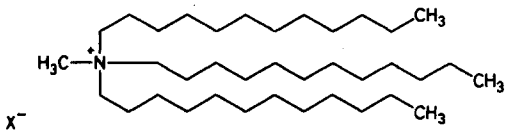

5

c,8-lactone [8]) and cobester-*c*-lactone (*a,b,d,e,f,g*-hexamethyl *Coα,Coβ*-dicyanocobyrinate *c*,8-lactone [9]). Reduction of the latter with Zn in AcOH/benzene 1:7 (using a modification [10] of a procedure from *Gossauer*'s laboratory [11][12] and of earlier

work (see discussions in [9])) led to cobester-*c*-monoacid **6** (*a,b,d,e,f,g*-hexamethyl *c*-hydrogen *Coα,Coβ*-dicyanocobyrinate). The mixed anhydride from **6** and 2,2,2-trichloro-1,1-dimethylethyl chloroformate was esterified with 1-octadecanol to produce the octadecyl-cobester **1** (92% yield from **6** after chromatographic purification). The product **1** was identified spectroanalytically. Treatment of **1** with CF_3CO_2H in dry $CHCl_3$, followed by aqueous workup, gave the *Co*-aqua-*Co*-cyano-cobyrinate **2** as a (*ca.* 2:1) mixture of the coordination isomers **2a** and **2b**. Photooxygenation of **1**, sensitized by methylene blue (MB), resulted in the two dioxosecocobyrinates **3** (octadecyl-5,6-dioxosecocobester) and **7** (octadecyl-14,15-dioxosecocobester) which were separated and purified by chromatography (combined yield 76%; ratio 2.2:1). This result is similar to that of the photooxygenation of 'cobester' (heptamethyl *Coα,Coβ*-dicyanocobyrinate [13][14]) described recently [15]. The structures of the secocorrinoid complexes **3** and **7** were assigned from the ^{1}H-NMR and FAB-MS spectra.

Anion selectivities were observed potentiometrically by the separate-solution method [16], and the results are given in *Fig. 1*. The values $K^{pot}_{Cl,X}$ express the preference by the membrane for the anion X^- relative to Cl^-. The selectivities induced in PVC/BBPA-membranes by the corrinoid Co(III)-complexes **1** and **2** were compared to those of other components (octadecyl-5,6-dioxosecocobester **3**, cholestano-cobaloxime **4** [6], and the lipophilic quarternary ammonium salt **5**) and to the selectivity of a blank membrane (last column in *Fig. 1*). The Co(III)-complexes **1** and **2** induce selectivities which deviate clearly and characteristically from those of classical anion exchanger membranes containing **5**. As expected, the membranes with **1**, **2**, and **5** exhibit a *Nernstian* response for changes in the activities of the most preferred anions (range $3 \cdot 10^{-6}$ to 10^{-1}M, *Fig. 2*).

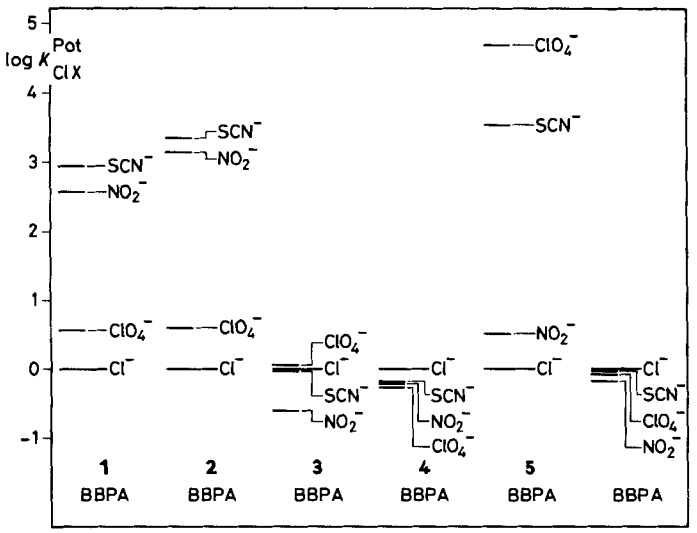

Fig. 1. *Selectivity factors, log* $K^{pot}_{Cl,X}$, *for solvent polymeric membranes with bis(1-butylpentyl)adipate (BBPA) as membrane solvent.* A ligand-free membrane (last column) is compared with membranes containing different components (**1–5**) (separate-solution method, TRIS-buffered solutions of 0.1M sodium salts, pH 7.45, 20°).

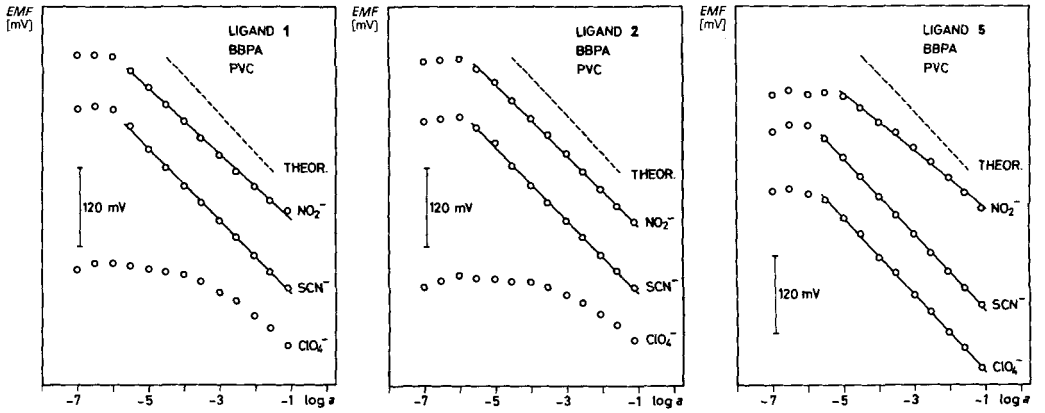

Fig. 2. EMF *response of liquid-membrane electrodes based on the ligands* **1**, **2**, *and* **5** *to different activities* a *of the anions indicated (sodium salts).* Solid lines represent experimental slopes of the electrode response.

The compounds **3** and **4** do not significantly change the selectivity relative to the unmodified membrane, and obviously are acting neither as anion exchangers nor as anion carriers. This is consistent with the typically slow ligand-exchange rate for analogues of **4** [5] and apparently for **3** (where evidence from preparative experiments led to the expectation of considerable inertness of the Co(III)-center). In contrast, the corrinoid Co(III)-complexes **1** and **2** function as selective anion carriers. This is in agreement with the typical behaviour of vitamin B_{12} derivatives which are known to exhibit exceptionally fast exchange kinetics for axial ligands at the Co(III)-center [5][17]. In addition, the rather high preference of NO_2^- over ClO_4^- by **1** and **2** *(Fig. 1)* correlates with the sequence of the equilibrium constants for the substitution of coordinated H_2O in aquacobalamin by NO_2^- and ClO_4^-, respectively [5].

The UV/VIS spectra of membranes with **1** and **2** indicate that both (**1** and **2**) undergo a structural change, presumably involving a ligand-exchange reaction. A reconditioning of the membrane with an aqueous NaCN solution (*ca.* 0.01 mol/l) indeed restored a spectrum corresponding to the octadecyl-cobester **1**.

According to the data presented here, the Co(III)-corrins **1** and **2**, when incorporated into PVC membranes with BBPA as plasticizer, undergo exchange of axial ligands and exhibit the behaviour of highly selective carriers for SCN^- and NO_2^-.

We are grateful to *C. Nussbaumer* for helpful discussions, to Professor Dr. *A. Eschenmoser* for support of this work and to Professor Dr. *J. Rétey* for a generous gift of the cholestano-cobaloxime. We acknowledge financial support by the *Swiss National Science Foundation*, by an ETH-Z research grant, by *Corning LTD*, Sudbury, and by *F. Hoffmann-La Roche & Co. AG*, Basel.

Experimental Part

General. Abbreviations: MB, methylene blue; BBPA, bis(1-butyl-pentyl) adipate; PVC, poly(vinyl chloride); TRIS, 2-amino-2-hydroxymethyl-1,3-propane-diol. TLC: on plates coated with silica gel *(Merck* Art. *5721)*. Chemicals and solvents: Cobester-*c*-monoacid **6** was prepared using a modification [10] of the published procedure [11]; CH_2Cl_2 (dry) *Fluka, puriss.*, filtered through aluminum oxide (*Woelm, B.* Akt. I) before use; Et_3N: *Fluka, puriss.*, distilled from CaH_2 *(Fluka, purum)*; 2,2,2-trichloro-1,1-dimethylethyl chloroformate: *Fluka, puriss.*; MB: PhHv; $CHCl_3$: *Fluka, puriss. p.a.*, filtered through aluminum oxide before use; CF_3CO_2H: *Fluka, purum*, distilled before use; $NaClO_4$: *Fluka, purum*; CD_3OD: *Fluka, puriss.* > 99.8% D; MeOH(HCN): means 1% HCN in MeOH; solvents (general): techn. grade, redistilled. *EMF*-measurements: deionized H_2O, doubly distilled from quartz vessels; BBPA: *Fluka, purum;* PVC: *Lonza AG*, Visp, S 704 'hochmolekular' (now available from *Fluka*); TRIS: *Fluka, puriss. p.a.;* H_2SO_4, conc.: *Merck, p.a.;* tri(dodecyl)methylammonium chloride: *Polysciences Inc.*, Warrington, PA 18976; $NaClO_4$: *Merck, p.a.;* NaSCN: *Fisher Scientific Co.*, Fair Lawn, New Jersey; NaCl: *Merck, p.a.;* $NaNO_2$: *Merck*, 'reinst'. UV/VIS: *Perkin-Elmer PE 555* or *Uvikon 810;* in MeOH/HCN (0.05%); citation of λ_{max} (log ε) in nm. CD: *Jobin-Yvon Mark III;* in MeOH/HCN (0.05%); wavelength of the extrema λ_m and of the zero passages λ_o in nm (molar decadic circular dichroism [$\Delta\varepsilon$]). IR: *Perkin-Elmer PE 125;* in $CHCl_3$; cm^{-1}, relative intensities (*s*, *m*, and *w* denote strong, medium, and weak, respectively). ^{1}H-NMR: *Bruker WM-300;* in $CDCl_3$; 300.14 MHz; TMS internal reference, chemical shifts in ppm with δ (TMS) = 0; coupling constants *J* in Hz. ^{13}C-NMR: *Bruker WM-300;* in $CDCl_3$; 75.47 MHz; TMS internal reference, chemical shifts in ppm with δ (TMS) = 0; multiplicities from the off-resonance decoupled spectrum. Fast-atom-bombardment(FAB) MS: *Kratos AEI MS-50* fitted with *M*-scan FAB-system; Ar bombardment at 8–10 kV.

***EMF*-Measurements.** The solvent polymeric membranes were prepared according to [18] using 1% *(w/w)* ligand, 66% *(w/w)* BBPA, and 33% *(w/w)* PVC. Cell assemblies of the following type were used: Hg; Hg_2Cl_2, KCl (satd.)|3M KCl|sample solution‖membrane‖0.01M NaCl, AgCl; Ag. For details on the cell assembly and *EMF*-measuring technique see [18]. Changes in the liquid junction potential and the activity coefficients were calculated with parameters given in [19][20]. The selectivity factors, log $K^{pot}_{Cl,X}$, were obtained by the separate-solution method [16] in 0.1M solutions of the corresponding sodium salts. The solutions were buffered using 0.01M TRIS and adjusted to pH 7.45 ± 0.05 with conc. H_2SO_4. The electrode functions were measured in unbuffered solutions. For the measurement of the SCN^- and ClO_4^- electrode response, the anion-exchanger membrane (based on **5**, initially with Cl^- as the counterion) was reconditioned for two days in 0.1M NaSCN and $NaClO_4$, respectively. All measurements were performed at 20 ± 0.5°C.

Syntheses. a,b,d,e,f,g-*Hexamethyl* c-*Octadecyl* Coα, Coβ-*Dicyanocobyrinate* **1**. Cobester-*c*-monoacid **6** (85 mg, 79.1 μmol) [10] was dissolved in dry CH_2Cl_2 (2 ml) under N_2, the solvent removed under vacuum, dried CH_2Cl_2 (10 ml) added under N_2, and the solution cooled externally with ice/H_2O/NaCl (−10°). Then, 2,2,2-trichloro-1,1-dimethylethyl chloroformate (22 mg, 90 μmol) and Et_3N (70 μl, 500 μmol) were added, and the cooled solution was stirred magnetically for 15 min and warmed up to r.t. Then, 750 mg (2.8 mmol) of 1-octadecanol were added, and the mixture was heated under reflux for 18 h. After cooling to r.t., it was transferred to the head of a column (3 × 25 cm; 100 g silica gel, *Merck 60* Art. *9385*). Excess 1-octadecanol was washed out with 300 ml of CH_2Cl_2, then the corrinoid compounds were eluted with CH_2Cl_2/MeOH(HCN) 98:2. The product fraction was shaken with 50 ml of aq. $NaHCO_3$ (containing 250 mg of KCN) and dried by filtration through dry cotton. After evaporation of the solvents at r.t., 96.5 mg (92%) of **1** was obtained as a violet-red residue, that was uniform by TLC (5.9 mg of **6** were also reisolated). It was converted into a powder by precipitation in hexane and dried (high vacuum, r.t., 2 h). UV/VIS ($c = 2.47 \cdot 10^{-5}$ mol/l): 266 (sh, 3.81), 277 (3.98), 310 (3.91), 351 (sh, 4.09), 368 (4.41), 385 (sh, 3.99), 418 (3.25), 474 (sh, 3.39), 504 (sh, 3.69), 543 (3.87), 582 (3.97). CD ($c = 2.47 \cdot 10^{-5}$ mol/l): 245 (sh, − 9.11), 252 (− 11.1), 280 (0.61), 308 (− 8.70), 327 (− 5.67), 347 (− 9.92), 367 (− 7.08), 394 (18.2), 426 (10.7), 495 (− 1.62), 537 (− 1.82), 581 (− 3.04); λ_o = 235, 270, 289, 374, 458. IR (4%): 2125*w*, 1733*s*, 1582*s*, 1503*s*, 1470*m*, 1440*s*, 1405*m*, 1395*m*, 1370*m*, 1355*m*, *etc.* ^{1}H-NMR: 0.88 (*t*, *J* = 7, 3H, $CH_3(CH_2)_{17}$); 1.21, 1.30, 1.35, 1.37, 1.51, 1.57, 2.19, 2.23 (8*s*, $8CH_3$) superimposed by 1.26 (br. *s*, *ca.* 30H) and 1.0–2.77 (*m*) – in total *ca.* 78H; 2.80–2.89 (*m*, 1H); 3.01 (*dd*, 1H, *J* = 4.5, 6.5, H–C(13)); 3.47 (*dd*, 1H, *J* = 8, 5, H–C(8)); 3.63, 3.66, 3.68, 3.69, 3.72, 3.76 (6*s*, 6 $COOCH_3$) superimposed by 3.78–3.9 (*m*, 2H, H–C(3), H–C(19)) – in total 20H; 4.07 (*t*, *J* = 7, 2H); 5.58 (*s*, 1H, H–C(10)). ^{13}C-NMR: 14.2, 15.3, 16.0, 17.0, 18.5, 19.2, 19.8, 22.1 (8*q*, $8CH_3$); 22.7, 25.0, 25.7, 26.0, 26.6, 28.6, 29.4 (double int.), 29.7 (*ca.* 10-fold int.), 30.7, 31.2 (double int.), 31.9 (double int.), 32.6, 33.7 (13*t*, 25C); 39.3 (*d*, C(18)); 41.1, 42.4 (2*t*, C(2'), C(7')); 45.6, 47.0, 48.7 (3*s*, C(2), C(7), C(12)); 51.6 (double int.), 51.8 (triple int.), 52.4 (3*q*, 6 $COOCH_3$); 53.6, 54.1, 56.6 (3*d*, C(3), C(8),

C(13)); 58.3 (*s*, C(17)); 64.9 (*t*, $CH_3(CH_2)_{16}CH_2$); 74.8 (*d*, C(19)); 82.6 (*s*, C(1)); 91.3 (*d*, C(10)); 102.1, 103.6 (2*s*, C(5), C(15)); 134.2, 136.5 (2*s*, 2CN); 163.4, 163.7 (2*s*, C(6), C(14)); 170.7, 171.5, 171.7, 172.0, 172.8, 172.9, 173.5, 173.9, 175.3, 175.6, 176.2 (11*s*). MS (FAB): 1328 (9), 1327 (20), 1326 (27, M^+); 1303 (14), 1302 (32), 1301 (70), 1300 (100, M^+–CN), 1299 (38); 1275 (28); 1274 (33, M^+–2CN); 1241 (10); 1214 (7); 1186 (5); 988 (4, M^+–CN–$C_{20}H_{40}O_2$)[1]); 962 (4, M^+–2CN–$C_{20}H_{40}O_2$)[1]); 904 (5); 876 (5, M^+–2CN–$C_{24}H_{46}O_4$); 802 (3, M^+–2CN–$C_{27}H_{52}O_6$); *etc.*

a,b,d,e,f,g-*Hexamethyl* c-*Octadecyl* Co-*Aqua*-Co-*cyanocobyrinate Perchlorate* (**2a**/**2b**). Octadecyl-cobester **1** (18.6 mg, 14 μmol) was dissolved in 1.5 ml of dry $CHCl_3$ and treated with 3 μl of CF_3CO_2H and the dark red solution stirred magnetically at r.t. for 7 min under N_2. A colour change towards bright red was observed. The solution was concentrated to about ½ of its original volume (high vacuum, r.t.). $CHCl_3$ (*ca.* 1 ml) was added, and ½ of the solvent was removed again (to remove HCN). The remaining solution was transferred to a separating funnel containing 40 ml of CH_2Cl_2, 40 ml of aq. phosphate buffer (1 mol/l, at pH 3.0), and *ca.* 500 mg of $NaClO_4$. Vigorous shaking led to a further change in colour to orange red. The org. phase was separated from the colourless aq. phase, filtered through dried cotton and evaporated (r.t.). After drying (high vacuum, r.t., 16 h), the red residue was analyzed (^{1}H-NMR) as a mixture of **2a**/**2b**. UV/VIS (benzene, λ_{max} (rel. int.)): 325 (0.69), 357 (1.00), 409 (0.30), 490 (0.40), 520 (0.33). IR (4%): 2140*w*, 1735*s*, 1620*w*, 1580*s*, 1500*s*, 1440*s*, 1350*m*, 1240*s*, 1150*s*, 1040*s*, *etc.* ^{1}H-NMR: 0.88 (*t*, *J* = 7, 3H); 1.17–2.80 (*m*) superimposed by 1.18, 1.25 (intense, br.), 1.30, 1.39, 1.45, 1.55, 1.67, 2.32, 2.33, 2.35, 2.39 (11*s*) – in total *ca.* 80H; 3.07 (*m*, 1H), 3.40 (*m*, 1H), 3.61, 3.63, 3.65, 3.67, 3.68, 3.70, 3.72, 3.74, 3.78, 3.79 (10*s*, 19H (*m* superimposed)); 3.88 (*m*, 1H); 4.02–4.40 (*m*, 3H); 6.45/6.48 (2*s*, 1H)[2]).

a,b,d,e,f,g-*Hexamethyl* c-*Octadecyl* Coα,Coβ-*Dicyano-5,6-dioxo-5,6-secocobyrinate* (**3**). Octadecyl-cobester **1** (23.5 mg, 17.7 μmol) was dissolved in 2.5 ml of CD_3OD containing 0.1 mg of MB and transferred to a *Schreiber* photoreactor (see *Fig. 2* in [15]) under O_2. The reaction vessel was immersed into a H_2O/ice cooling bath and, while O_2 purging was continued, it was irradiated for 30 min through a $Na_2Cr_2O_7$ filter solution with the light of a 15V/150W lamp *(BLV Licht- und Vakuumtechnik)* operated at 7 V and positioned at a distance of 8 cm (see exper. details in [15]). The reaction mixture was then transferred and the solvents evaporated at r.t. The residue was separated on 2 TLC plates (CH_2Cl_2/MeOH(HCN) 95:5) into a red, less polar and an orange, polar fraction. The 2 fractions were scraped and eluted with MeOH(HCN). The polar fraction was taken up in 50 ml of CH_2Cl_2 and shaken with 50 ml of dil. aq. $NaHCO_3$ (containing 50 mg of KCN). The org. phase was separated, filtered through cotton and evaporated to dryness (r.t.) to give 12.3 mg (52%) of **3** as an orange residue, uniform by TLC. The less polar fraction (mixture **1**/**7**) was dried, dissolved in 10 ml of $CHCl_3$ containing 50 μl of CF_3CO_2H under N_2, and stirred at r.t. for 10 min. The solvents were evaporated (r.t.), and the red residue was separated on a TLC plate as before (CH_2Cl_2/MeOH 95:5 free of HCN) into a less polar orange fraction (of **7**) and a mixture of 2 red, polar compounds (corresponding to **2a**/**2b**), which were worked up as described above for **3** giving 3.3 mg (14%) of **1** and 5.8 mg (24%) of the isomeric a,b,d,e,f,g-*hexamethyl* c-*octadecyl 14,15-dioxo-14,15-seco-cobyrinate* (**7**). The latter was uniform by TLC and structurally assigned by comparison of its spectral data with those of **3**. Data of **3**: UV/VIS ($c = 3.38 \cdot 10^{-5}$mol/l): 272 (sh, 4.05), 290 (sh, 3.96), 314 (sh, 3.99), 325 (4.03), 366 (sh, 3.45), 480 (3.99). IR (4%): 2127*w*, 1733*s*, 1557*m*, 1530*m*, 1499*m*, 1460*m*, 1440*s*, 1405*m*, 1390*m*, 1370*m*, *etc.* ^{1}H-NMR: 0.88 (*t*, 3H, *J* = 7); 0.99, 1.20, 1.24, 1.26 (br., intense), 1.29 (double int.), 1.98, 2.21, 2.65 (8*s*) superimposed by 1.10–3.10 (*m*) – in total 80H; 3.24 (*d*-like, 1H); 3.57, 3.66, 3.68, 3.69, 3.72, 3.77 (6*s*, 6 $COOCH_3$) superimposed by 3.7–3.9 (*m*) – in total 20H; 4.09 (*m*, 2H); 5.56 (*s*, 1H, H–C(10)). MS (FAB): 1359 (13), 1358 (15, M^+); 1345 (5); 1334 (32), 1333 (64), 1332 (100, M^+–CN), 1331 (26); 1318 (7); 1308 (7), 1307 (16), 1306 (23, M^+–2CN), 1305 (10), 1304 (11); 1301 (6); 1274 (6), 1272 (6); 1246 (7); 1089 (2), 1063 (2); 1034 (2); 1010 (7), 1009 (12, M^+–2CN–297)[3]), *etc.* Data of **7**: UV/VIS ($c = 3.88 \cdot 10^{-5}$ mol/l): 272 (sh, 3.92), 289 (sh, 3.81), 314 (sh, 3.87), 326 (3.96), 366 (sh, 3.20), 480 (3.92), 560 (br. sh, *ca.* 3.22). IR (4%): 2127*w*, 1730*s*, 1567*m*, 1535*m*, 1500*m*, 1465*m*, 1438*s*, 1405*m*, 1380*m*, *etc.* ^{1}H-NMR: 0.88 (*t*, *J* = 7, 3H); 1.25 (br.*s*, intense), 1.30 (double int.), 1.32, 1.33, 1.50, 2.11, 2.81 (7*s*) superimposed by 2.34/3.34 (*AB*, $J_{AB} = 15$, together 2H), 3.26 (*dd*, 1H) and 1.2–3.0 (*m*) – in total *ca.* 80H; 3.66, 3.665, 3.68, 3.69, 3.72, 3.74 (6*s*, 6 $COOCH_3$) – in total 19H (*m*/1H, hidden); 3.85 (*d*-like, 1H); 4.02 (*t*-like, 2H, $CH_3(CH_2)_{16}(CH_2)$; 4.96 (*d*, *J* = 8, 1H, H–C(19)); 5.53 (*s*, 1H, H–C(10)). MS (FAB): 1360 (7), 1359 (14), 1358 (23, M^+); 1345 (5); 1334 (30), 1333 (65), 1332 (100,

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[1]) Interpretation of $C_{20}H_{40}O_2$: octadecyl acetate fragment.

[2]) A *ca.* 2:1 mixture of the coordination isomers **2a** and **2b** (transformed into **1** by addition of HCN).

[3]) Interpretation: loss of ring-A fragment.

M^+–CN); 1318 (10); 1307 (14), 1306 (23, M^+–2CN); 1300 (9); 1273 (10), 1246 (7); 1049 (2); 1024 (10), 1023 (16, M^+–2CN–283)[4]); 1008 (4), 976 (3), 952 (5), 951 (7), *etc.*

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